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P O L S K I E T O W A R Z Y S T W O F I Z Y C Z N E

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PAŃSTWOWE WYDAWNICTWO NAUKOWE

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ON THE APPROACH TO EQUILIBRIUM OF SPIN WAVES SYSTEM. I.

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The author calculates the spin-spin relaxation time in ferromagnetics caused by pseudo-dipolar interactions between spins. Calculations are based on the spin wave theory in the form given by Dyson. Non Hermitian Hamiltonian in the ideal model of spin waves system is derived and transition probabilities in first approximation are calculated. In this approximation it appears that processes of splitting of one spin wave into two (and confluence of two into one) and of mutual scattering of two spin waves are the only possible ones. Kinetic equation taking into account these processes is derived and relaxation time is determined. Numerical values of relaxation time for spin waves with zero wave vector are calculated, showing that contribution to the line width of ferromagnetic resonance absorption from such spin waves is not important.

§ 1. Introduction

Relaxation phenomena in ferromagnetics are intimately connected with the line width in ferromagnetics resonance absorption experiments. Complete theoretical explanation of the observed line width and its temperature dependence is — in spite of many efforts in this direction — not yet achieved. Several relaxation mechanisms may contribute to the line width. The most important among them seems to be interactions between spin waves tending to establishment of thermodynamical equilibrium in spins system (Akhiezer 1946; Kasuya 1954a; Kaganov, Tsukernik 1958), interactions between “ferromagnetic” d -electrons and conduction electrons (Abrahams 1955, Mitchell 1957, Kasuya 1954b, Kondoh 1953), and interactions of spin waves with lattice vibrations (“phonons”) levelling spin system and lattice temperatures (Akhiezer 1946; Kittel Abrahams 1953; Sugihara 1953, Terasaki, Manari 1957; Kaganov, Tsukernik 1959 also Akhiezer et al. 1959). Another attempts to explain line width were also published (see for instance recent concise review of this question in V. Kranendonk; V. Vleck 1958).

The situation is thus quite complicated, relative importance of these various processes in real experimental conditions is not exactly known. It seems thus that

possibilities of improving the existing theoretical values of relaxation times by mathematically more rigorous treatment cannot be overlooked.

The purpose of the investigations presented here is to reexamine the theory of relaxation processes in spin waves system. Existing papers on the same problem (Akhiezer 1946, Kasuya 1954, Kaganov, Tsukernik 1958) are all based on Holstein-Primakoff's theory of spin wave interactions. Recently Dyson (1956 a, b) criticized the formalism of Holstein and Primakoff showing that: 1) spin-wave amplitude operators introduced by them do not have proper physical interpretation and 2) mathematical approximations indispensable for simplification of intricate Holstein — Primakoff's Hamiltonian are not always justified. In Dyson's papers more exact theory of spin wave interactions is given. In the present paper we take Dyson's treatment of spin waves as a starting point for calculation of relaxation times, hoping that values obtained in this way are more appropriate than the former ones.

§ 2. Hamiltonian

We shall discuss the relaxation of spin waves in perfect cubic crystals of a ferromagnetics. We start with the Heisenberg model of ferromagnetics. The s — d interactions will be completely neglected, although it is well known that the contribution to the line width caused by conduction electrons is by no means negligible in real ferromagnetic metals. Our task is merely to examine relaxation processes connected with direct interactions of spin waves.

We assume that each lattice point is determined by a lattice vector \vec{j} , let N be the total number of lattice sites in the crystal. Periodic boundary conditions are assumed. At each lattice point \vec{j} is situated spin vector $\vec{S}_j = (S_j^x, S_j^y, S_j^z)$ of magnitude S .

The Hamiltonian of the system consists of 3 terms:

1) Zeeman energy in a uniform external magnetic field H , directed along the z -axis of a frame of reference:

$$2\mu_B H \sum_j S_j^z \quad (2.1)$$

μ_B — Bohr magneton; —

2) isotropic exchange interaction with (positive) coupling constant J_{jk} (in practice $J_{jk} = J$, when \vec{j} and \vec{k} are nearest neighbour lattice sites and $J_{jk} = 0$ for other cases)

$$- \frac{1}{2} \sum_{j \neq k} J_{jk} \vec{S}_j \cdot \vec{S}_k \quad (2.2)$$

3) anisotropic interaction energy between spins. We adopt the lowest order anisotropic coupling i. e. the so called "pseudo-dipolar coupling" of the form (see: Van Vleck 1937, Van Kranendonk, Van Vleck, 1958):

$$\frac{1}{2} \sum_{j \neq k} D_{jk} [\vec{S}_j \cdot \vec{S}_k - 3 (\vec{S}_j \cdot \vec{e}_{jk}) (\vec{S}_k \cdot \vec{e}_{jk})] \quad (2.3)$$

wherein

$$\vec{e}_{jk} = (\vec{j} - \vec{k})/|\vec{j} - \vec{k}|$$

The pseudo-dipolar coupling arises from indirect effect of spin-orbit interaction; the coupling constant D_{jk} rapidly decreases with increasing distance between \vec{j} and \vec{k} , being significant only for nearest neighbour spins. The classical magnetic spin—spin interactions are also of the form (2.3), the coupling constant for these interactions is

$$D_{jk} = (2\mu_B)^2/|\vec{j} - \vec{k}|^3 \quad (2.4)$$

They are weaker than the former ones at nearest neighbours distance but have a long range character. For $S > 1/2$ higher multipole interactions can also be important, but we shall neglect them in this paper.

The total Hamiltonian is thus equal to

$$\mathcal{H} = L \sum_j \vec{S}_j^z - \frac{1}{2} \sum_{j \neq k} J_{jk} \vec{S}_j \cdot \vec{S}_k + \frac{1}{2} \sum_{j \neq k} D_{jk} [\vec{S}_j \cdot \vec{S}_k - 3 (\vec{S}_j \cdot \vec{e}_{jk}) (\vec{S}_k \cdot \vec{e}_{jk})] \quad (2.5)$$

where

$$L = 2\mu_B H \quad (2.6)$$

In the following considerations we shall often use the well known operators

$$\begin{aligned} S_j^+ &= S_j^x + iS_j^y \\ S_j^- &= S_j^x - iS_j^y \end{aligned} \quad (2.7)$$

and their Fourier transforms:

$$\begin{aligned} S_\lambda^+ &= N^{-\frac{1}{2}} \sum_j e^{i\vec{\lambda} \cdot \vec{j}} S_j^+ \\ S_\lambda^- &= N^{-\frac{1}{2}} \sum_j e^{i\vec{\lambda} \cdot \vec{j}} S_j^- \end{aligned} \quad (2.8)$$

§ 3. Formulation of the problem

We shall examine the processes of mutual scattering of spin waves, leading to establishment of a thermodynamical equilibrium state of spin system and we shall find the spin-spin relaxation time.

As the basis of our calculations we adopt Dysons (1956 a, b) theory of spin wave interactions.

According to Dyson (1956 a) we define the spin wave state containing a_λ spin waves with wave vector $\vec{\lambda}$ by:

$$|a\rangle = \prod_\lambda (2S)^{-\frac{1}{2} a_\lambda} (a_\lambda!)^{-\frac{1}{2}} (S_\lambda^+)^{a_\lambda} |0\rangle \quad (3.1)$$

where the ground state fulfils the condition:

$$S_\lambda^- |0\rangle = 0 \quad (3.2)$$

The states $|a\rangle$ (with the exception of case $\sum_{\lambda} a_{\lambda} = 1$) are not orthogonal to each other. The spin waves are thus not independent, some constraints are imposed on them — the so called by Dyson kinematical interactions.

In order to avoid mathematical difficulties connected with kinematical interactions and manifesting themselves in nonorthogonality of states $|a\rangle$ Dyson introduces another complete set of orthonormal states $|a\rangle$, being in one-to-one correspondence with the primary set of states $|a\rangle$. The “ideal spin wave states” $|a\rangle$ are defined by:

$$|a\rangle = \prod_{\lambda} (a_{\lambda}!)^{-\frac{1}{2}} (a_{\lambda}^{\dagger})^{a_{\lambda}} |0\rangle \quad (3.3)$$

$$a_{\lambda} |0\rangle = 0 \quad (3.4)$$

where a_{λ}^{\dagger} , a_{λ} are the well known harmonic oscillator operators (creation a_{λ}^{\dagger} and annihilation a_{λ} operators), satisfying the commutation rules:

$$[a_{\lambda}, a_{\mu}^{\dagger}] = \delta_{\lambda\mu} \quad [a_{\lambda}, a_{\mu}] = [a_{\lambda}^{\dagger}, a_{\mu}^{\dagger}] = 0 \quad (3.5)$$

and

$$a_{\lambda}^{\dagger} a_{\lambda} |a\rangle = a_{\lambda} |a\rangle \quad (3.6)$$

or formally

$$a_{\lambda}^{\dagger} a_{\lambda} = a_{\lambda}$$

Starting with the Hamiltonian \mathcal{H} (2.5), expressed in terms of operators S_{λ}^{\dagger} , S_{λ}^{-} , S_{λ}^z we can — following the method given by Dyson — construct an operator $\widetilde{\mathcal{H}}$ in the ideal spin waves space (“ideal model”), operating on the ideal states $|a\rangle$ in the same way as does Hamiltonian \mathcal{H} on the physical states $|a\rangle$.

The analysis given below leads to an other simple formal way of constructing $\widetilde{\mathcal{H}}$, more useful than Dyson’s original one in cases of complicated Hamiltonian.

Let Ω be an Hermitian operator in the physical model and $|\psi\rangle$ any physical state. In the ideal model the state $|\psi\rangle$ is replaced by the ideal state $|\psi\rangle$. The state $(\bar{\psi}|$ adjoint to $|\psi\rangle$ in the ideal model is defined according Dyson (1956 b) by $(\bar{\psi}| = (\psi|F$ where the operator F is the so called “indefinite metric tensor”. The correspondence between matrix elements of an operator Ω in the physical and ideal models is given by equation (Dyson, 1956 b):

$$\langle \varphi | \Omega | \psi \rangle = (\bar{\varphi} | \widetilde{\Omega} | \psi) = (\varphi | F \widetilde{\Omega} | \psi) \quad (3.7)$$

(symbol \sim means, that the quantity in question refers to ideal model). It is easy to verify, that operator Ω , Hermitian in the physical model, satisfies in the ideal model the condition (Dyson, 1956 b)

$$F \widetilde{\Omega} = \widetilde{\Omega}^{\dagger} F \quad (3.8)$$

($\widetilde{\Omega}^{\dagger}$ denotes the Hermitian adjoint of the operator $\widetilde{\Omega}$) i. e. $\widetilde{\Omega}$ is self-adjoint with respect to metric F .

The explicit expression for the metric tensor F can be given using a particular set of states. Let us take a set of integers $0 \leq u_j \leq 2S$, corresponding to lattice points \vec{j} . We define, according to Dyson (1956 a, eq. (30)), a complete and orthogonal (but not normalized) set of states with localized spin deviations:

$$|u\rangle = \prod_j (2S)^{-\frac{1}{2}u_j} (u_j!)^{-\frac{1}{2}} (S_j^+)^{u_j} |0\rangle \quad (3.9)$$

In the ideal model the state $|u\rangle$ is connected with the ideal state

$$|u\rangle = \prod_j (u_j!)^{-\frac{1}{2}} (\eta_j^+)^{u_j} |0\rangle \quad (3.10)$$

describing a collection of harmonic oscillators attached to lattice points \vec{j} , where oscillator amplitudes η_j^+ (creation operators) and η_j (annihilation operators) satisfy commutation rules

$$[\eta_j, \eta_k^+] = \delta_{jk} \quad [\eta_j, \eta_k] = [\eta_j^+, \eta_k^+] = 0 \quad (3.11)$$

and the integer u_j is the eigenvalue of operator $\eta_j^+ \eta_j$.

By (3.7) we have (Dyson, 1956 b):

$$(u|F|v) = \langle u|v\rangle \quad (3.12)$$

From the other hand from (3.9) follows (Dyson, 1956 a, eq. (31))

$$\langle u|v\rangle = F_u \delta_{uv} \quad (3.13)$$

where $\delta_{uv} = \prod_j \delta_{u_j, v_j}$ (δ_{u_j, v_j} is the Kronecker symbol) and

$$F_u = \prod_j F(u_j) \quad F(u_j) = 1 \cdot \left(1 - \frac{1}{2S}\right) \dots \left(1 - \frac{u_j - 1}{2S}\right) \quad (3.14)$$

From eqs. (3.12), (3.13) it follows that:

$$(u|F|v) = F_u \delta_{uv}$$

This is equivalent to:

$$(u|F = F_u (u| \quad (3.15)$$

It is not hard to prove now, that

$$(u|F_u = (0| \left[\prod_j \eta_j^{u_j} (u_j!)^{-\frac{1}{2}} \right] F = (0| \prod_j \left[\left(1 - \frac{1}{2S} \eta_j^+ \eta_j\right) \eta_j \right]^{u_j} (u_j!)^{-\frac{1}{2}} \quad (3.16)$$

It is thus evident, that correspondence

$$\begin{aligned} |u\rangle &\rightarrow |u\rangle \\ \langle v| &\rightarrow \langle \bar{v}| = \langle v| F \end{aligned} \quad (3.17)$$

can be realized by replacing operators S_j^+ , S_j^- , S_j^z by η_j^+ , η_j according to the rules (c. f. Maleev, 1957):

$$\begin{aligned} S_j^- &\rightarrow (2S)^{\frac{1}{2}} \left(1 - \frac{1}{2S} \eta_j^+ \eta_j \right) \eta_j \\ S_j^+ &\rightarrow (2S)^{\frac{1}{2}} \eta_j^+ \\ S_j^z &\rightarrow \eta_j^+ \eta_j - S \end{aligned} \quad (3.18)$$

Replacing operators S_j^+ , S_j^- , S_j^z in Hamiltonian \mathcal{H} (2.1) by η_j^+ , η_j we formally get the operator $\widetilde{\mathcal{H}}$ in the ideal model. To pass over from localized oscillators to spin waves the following Fourier transformations must be performed:

$$\begin{aligned} \eta_j^+ &= N^{-\frac{1}{2}} \sum_{\lambda} e^{-i\vec{\lambda} \cdot \vec{j}} \alpha_{\lambda}^+ \\ \eta_j &= N^{-\frac{1}{2}} \sum_{\lambda} e^{i\vec{\lambda} \cdot \vec{j}} \alpha_{\lambda} \end{aligned} \quad (3.19)$$

It is easy to prove, that (3.18) and (3.19) are equivalent to

$$\begin{aligned} S_{\lambda}^+ &\rightarrow (2S)^{\frac{1}{2}} \alpha_{\lambda}^+ \\ S_{-\lambda}^- &\rightarrow (2S)^{\frac{1}{2}} [\alpha_{\lambda} - (2SN)^{-1} \sum_{\kappa\mu} \alpha_{\kappa+\mu-\lambda}^+ \alpha_{\kappa} \alpha_{\mu}] \end{aligned} \quad (3.20)$$

In transforming Hamiltonian (2.1) by means of (3.20) some approximations are used which are discussed below. Sums of the form

$$N^{-1} \sum_{j \neq k} D_{jk} e^{-i(\vec{\lambda} \cdot \vec{j} + \vec{\mu} \cdot \vec{k})}$$

may be written as

$$N^{-1} \sum_{\vec{k}} e^{-i(\vec{\lambda} + \vec{\mu}) \cdot \vec{k}} \sum_{j(j \neq k)} D_{jk} e^{-i\vec{\lambda} \cdot (\vec{j} - \vec{k})}$$

The pseudo-dipolar coupling constant is a function of $h = |\vec{j} - \vec{k}|$ only, rapidly decreasing with an increase of h . If we neglect the lattice points lying on the ends of the crystal the sum $\sum_j D_{jk} \exp [-i\vec{\lambda} \cdot (\vec{j} - \vec{k})]$ does not depend¹ on \vec{k} (compare Holstein, Primakoff, 1940; page 1102).

Thus we have approximately:

$$N^{-1} \sum_{j \neq k} D_{jk} e^{-i(\vec{\lambda} \cdot \vec{j} + \vec{\mu} \cdot \vec{k})} = \delta(\vec{\lambda} + \vec{\mu}) \sum_{h \neq 0} D(h) e^{-i\vec{\lambda} \cdot \vec{h}} \quad (3.21)$$

¹ The formal grounds for this approximation lies in assumption of periodic boundary conditions. On the other hand theoretical and experimental evidence points out that such approximations must be used with some care — compare for instance Kittel 1958.

After treating in this way other sums and after rearranging the elements the quasi-Hamiltonian takes the form:

$$\begin{aligned}
 \widetilde{\mathcal{H}} = & N(P_0^z S^2 - LS) + \sum_{\lambda} (R_{\lambda}^+ + R_{\lambda}^- - 2SP_0^z + L) \alpha_{\lambda}^+ \alpha_{\lambda} + \sum_{\lambda} (Q_{\lambda}^+ \alpha_{\lambda}^+ \alpha_{-\lambda}^+ + \\
 & + Q_{\lambda}^- \alpha_{\lambda} \alpha_{-\lambda}) - (2SN^{-1})^{\frac{1}{2}} \sum_{\lambda \varrho} (T_{\lambda}^- \alpha_{\lambda}^+ \alpha_{\varrho-\lambda}^+ \alpha_{\varrho} + T_{\lambda}^+ \alpha_{\lambda} \alpha_{\varrho-\lambda} \alpha_{\varrho}^+) - \\
 & - (2SN)^{-1} \sum_{\lambda \varrho \sigma} (R_{\lambda}^+ + R_{\lambda}^- - 2SP_{\lambda-\varrho}^z) \alpha_{\varrho+\sigma-\lambda}^+ \alpha_{\lambda}^+ \alpha_{\varrho} \alpha_{\sigma} - \\
 & - (SN)^{-1} \sum_{\lambda \varrho \sigma} Q_{\lambda}^- \alpha_{\lambda+\varrho+\sigma}^+ \alpha_{\lambda} \alpha_{\varrho} \alpha_{\sigma} + (2SN^3)^{-\frac{1}{2}} \sum_{\lambda \mu \nu \varrho} T_{\lambda}^+ \alpha_{\mu+\nu+\lambda}^+ \alpha_{\mu} \alpha_{\nu} \alpha_{\varrho-\lambda}^+ \alpha_{\varrho} + \\
 & + (2SN)^{-2} \sum_{\lambda \mu \nu \varrho \sigma} Q_{\lambda}^- \alpha_{\mu+\nu+\lambda}^+ \alpha_{\mu} \alpha_{\nu} \alpha_{\varrho+\sigma-\lambda}^+ \alpha_{\varrho} \alpha_{\sigma}
 \end{aligned} \quad (3.22)$$

where the coefficients are defined by

$$\begin{aligned}
 Q_{\lambda}^{\pm} &= \frac{1}{2} S (P_{\lambda}^x - P_{\lambda}^y \pm 2iT_{\lambda}^{xy}) \\
 R_{\lambda}^{\pm} &= \frac{1}{2} S (P_{\lambda}^x + P_{\lambda}^y \pm 2iT_{\lambda}^{xy}) \\
 T_{\lambda}^{\pm} &= T_{\lambda}^{xx} \pm iT_{\lambda}^{yz}
 \end{aligned} \quad (3.23)$$

wherein

$$\begin{aligned}
 P_{\lambda}^{\xi} &= -\frac{1}{2} \sum_{h \neq 0} [J(h) - D(h) + 3D(h) h_{\xi}^2/h^2] e^{-i\vec{\lambda} \cdot \vec{h}} \\
 T_{\lambda}^{\xi\eta} &= \frac{3}{2} \sum_{h \neq 0} D(h) (h_{\xi} h_{\eta}/h^2) e^{-i\vec{\lambda} \cdot \vec{h}}
 \end{aligned} \quad \xi, \eta = x, y, z \quad (3.24)$$

Summations over \vec{h} extend on all neighbours of the lattice point $\vec{j} = 0$, practically we can, however, consider only the contributions coming from nearest neighbours and neglect others.

It is evident from (3.22) that the quasi-Hamiltonian is not Hermitian. The method of calculation using this unusual quantity will be explained below.

The quasi-Hamiltonian $\widetilde{\mathcal{H}}$ may be divided into "nearly" diagonal part $\widetilde{\mathcal{H}}_0$ and interaction Hamiltonian $\widetilde{\mathcal{H}}_I$, which will be of primary importance in our calculations.

$$\widetilde{\mathcal{H}} = E_0 + \widetilde{\mathcal{H}}_0 + \widetilde{\mathcal{H}}_I \quad (3.25)$$

where $E_0 = N(P_0^z S^2 - LS)$ and

$$\widetilde{\mathcal{H}} = \sum_{\lambda} (R_{\lambda}^+ + R_{\lambda}^- - 2SP_0^z + L) \alpha_{\lambda}^+ \alpha_{\lambda} + \sum_{\lambda} (Q_{\lambda}^+ \alpha_{\lambda}^+ \alpha_{-\lambda}^+ + Q_{\lambda}^- \alpha_{\lambda} \alpha_{-\lambda}) \quad (3.26)$$

The coefficients $R_{\lambda}^+ + R_{\lambda}^- - 2SP_0^z$ are in first approximation proportional to the exchange integral between nearest neighbours J , while Q_{λ} are proportional to the pseudo-dipolar coupling constant D . As $D|J| \ll 1$ the Q_{λ} term is a small correction. We are interested in energy of spin waves only in first approximation thus the correction terms will be neglected (for more detailed discussion see Appendix I).

In this approximation we have the energy ε_λ of spin wave with wave vector $\vec{\lambda}$:

$$R_\lambda^+ + R_\lambda^- - 2SP_0^z + L \cong S \sum_{h \neq 0} J(h) (1 - e^{-i\vec{\lambda} \cdot \vec{h}}) + L = \varepsilon_\lambda \quad (3.27)$$

In nearest neighbours approximation we get

$$\varepsilon_\lambda = L + JS(\gamma_0 - \gamma_\lambda) \quad (3.28)$$

wherein

$$\gamma_\lambda = \sum_{h \neq 0} e^{-i\vec{\lambda} \cdot \vec{h}} \quad (3.29)$$

and γ_0 is the coordination number of the lattice.

§ 4. Transition probabilities in the ideal model in first approximation

Let $|\psi\rangle$ be a time dependent state in the physical model, satisfying the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\psi\rangle = \mathcal{H} |\psi\rangle \quad (4.1)$$

The corresponding equation in the ideal model is (compare Dyson 1956 b, § 2)

$$i\hbar \frac{\partial}{\partial t} |\psi\rangle = \widetilde{\mathcal{H}} |\psi\rangle \quad (4.2)$$

where $|\psi\rangle$ is an ideal state corresponding to physical state $|\psi\rangle$. The equation adjoined with respect to the metric F to eq. (4.2) is

$$-i\hbar \frac{\partial}{\partial t} (\psi| F = (\psi| F \widetilde{\mathcal{H}} \quad (4.3)$$

where we have taken into account the eq. (3.8).

Equation (4.2) determining the vector of state $|\psi\rangle$ and eq. (4.3) determining the adjoined vector of state $(\psi| F$ form the starting point for our calculation of transition probability from one ideal state $|a\rangle$ (defined by eq. (3.3)) to another one.

The derivation of transition probability is well known and we quote here some important points of this calculations merely because some modifications are needed here in order to account for indefinite metric and non-Hermitian Hamiltonian.

We expand the state vectors $|\psi\rangle$, $(\psi| F$ into orthonormal set of states $|a\rangle$:

$$\begin{aligned} |\psi\rangle &= \sum_a |a\rangle (a|\psi) \\ (\psi| F &= \sum_a (\psi| F| a\rangle (a| \end{aligned} \quad (4.4)$$

with expansion coefficients depending on time. The probability that at some given time the system is in the state $|a\rangle$ is defined as:

$$(\psi|F|a)(a|\psi) \quad (4.5)$$

From eqs (4.2), (4.3) it follows that the quantity $(\psi|F|\psi) = \sum_a (\psi|F|a)(a|\psi)$ has a stationary value and thus can be normalized to unity.

According to eq. (3.25) the quasi-Hamiltonian $\widetilde{\mathcal{H}}$ (apart from constant E_0) may be broken into diagonal (and Hermitian) part $\widetilde{\mathcal{H}}_0$ and interactions part $\widetilde{\mathcal{H}}_I$. Denoting by ε_a the unperturbed energy of the state $|a\rangle$, given by the Schrödinger equation (compare (4.2)) with disregard of the $\widetilde{\mathcal{H}}_I$

$$\varepsilon_a |a\rangle = \widetilde{\mathcal{H}}_0 |a\rangle \quad (4.6)$$

and introducing other expansion coefficients $\bar{C}_a(t)$, $C_a(t)$ by

$$\begin{aligned} (a|\psi) &= C_a(t) e^{-\frac{i}{\hbar} \varepsilon_a t} \\ (\psi|F|a) &= \bar{C}_a(t) e^{\frac{i}{\hbar} \varepsilon_a t} \end{aligned} \quad (4.7)$$

we obtain from eqs (4.4), (4.2) and (4.3)

$$\begin{aligned} \frac{dC_a(t)}{dt} &= -\frac{i}{\hbar} \sum_b (a|\widetilde{\mathcal{H}}_I|b) C_b(t) e^{\frac{i}{\hbar} (\varepsilon_a - \varepsilon_b)t} \\ \frac{d\bar{C}_a(t)}{dt} &= \frac{i}{\hbar} \sum_b e^{-\frac{i}{\hbar} (\varepsilon_a - \varepsilon_b)t} \bar{C}_b(t) (b|\widetilde{\mathcal{H}}_I|a) \end{aligned} \quad (4.8)$$

As is well known equations (4.8) can be solved in first order approximation of the perturbation theory in the usual way (see for instance Schiff 1955). As a result we get the transition probability per unit of time from the ideal state $|a\rangle$ to the state $|b\rangle$

$$W_{ab} = \frac{2\pi}{\hbar} (a|\widetilde{\mathcal{H}}_I|b) (b|\widetilde{\mathcal{H}}_I|a) \delta(\varepsilon_a - \varepsilon_b) \quad (4.9)$$

It is worth noting here that W_{ab} evidently secures fulfilment of the principle of detailed balance in spite of non-Hermitian Hamiltonian $\widetilde{\mathcal{H}}$. In this case detailed balance follows from eq. (3.8), which replaces Hermiticity condition of the traditional derivation.

§ 5. Kinetic equation and relaxation time

We proceed now to the analysis of matrix elements involved in the expression (4.9) for transition probability. In the first place it is not difficult to see that some contributions to the transition probability W_{ab} vanish identically for all states

$|a\rangle$ and $|b\rangle$

$$(a| \sum_{\lambda q \sigma} Q_{\lambda}^{-} \alpha_{\lambda+q+\sigma}^{+} \alpha_{\lambda} \alpha_q \alpha_{\sigma} |b\rangle (b| \sum_{\lambda q \sigma} Q_{\lambda}^{-} \alpha_{\lambda+q+\sigma}^{+} \alpha_{\lambda} \alpha_q \alpha_{\sigma} |a\rangle = 0 \quad (5.1a)$$

$$(a| \sum_{\lambda \mu \nu q} T_{\lambda}^{+} \alpha_{\mu+\nu+\lambda}^{+} \alpha_{\mu} \alpha_{\nu} \alpha_{q-\lambda}^{+} \alpha_q |b\rangle (b| \sum_{\lambda \mu \nu q} T_{\lambda}^{+} \alpha_{\mu+\nu+\lambda}^{+} \alpha_{\mu} \alpha_{\nu} \alpha_{q-\lambda}^{+} \alpha_q |a\rangle = 0 \quad (5.1b)$$

$$(a| \sum_{\lambda \mu \nu q \sigma} Q_{\lambda}^{-} \alpha_{\mu+\nu+\lambda}^{+} \alpha_{\mu} \alpha_{\nu} \alpha_{q+\sigma-\lambda}^{+} \alpha_q \alpha_{\sigma} |b\rangle (b| \sum_{\lambda \mu \nu q \sigma} Q_{\lambda}^{-} \alpha_{\mu+\nu+\lambda}^{+} \alpha_{\mu} \alpha_{\nu} \alpha_{q+\sigma-\lambda}^{+} \times \\ \times \alpha_q \alpha_{\sigma} |a\rangle = 0 \quad (5.1c)$$

Thus in the approximation adopted here establishment of thermodynamic equilibrium in spin-wave system is secured by processes involving only 3 and 4 spin waves. Therefore, the interaction part $\tilde{\mathcal{H}}_I$ of the ideal Hamiltonian, determined by eqs (3.22) — (3.26) is in the present calculation equivalent to

$$\tilde{\mathcal{H}}_I' = \tilde{\mathcal{H}}_3 + \tilde{\mathcal{H}}_4 \quad (5.2)$$

where

$$\tilde{\mathcal{H}}_3 = - (2SN^{-1})^{\dagger} \sum_{\lambda q} (T_{\lambda}^{-} \alpha_{\lambda}^{+} \alpha_{q-\lambda}^{+} \alpha_q + T_{\lambda}^{+} \alpha_{\lambda} \alpha_{q-\lambda} \alpha_q^{+}) \quad (5.3)$$

$$\tilde{\mathcal{H}}_4 = - (2SN)^{-1} \sum_{\lambda q \sigma} (R_{\lambda}^{+} + R_{\lambda}^{-} - 2SP_{\lambda-q}^z) \alpha_{q+\sigma-\lambda}^{+} \alpha_{\lambda}^{+} \alpha_q \alpha_{\sigma} \quad (5.4)$$

a) Transition probabilities for processes with 3 spin waves

It is convenient to transform $\tilde{\mathcal{H}}_3$ of eq. (5.3) into more symmetrical form

$$\tilde{\mathcal{H}}_3 = \sum_{\lambda q} (A_{\lambda q}^{-} \alpha_{\lambda}^{+} \alpha_q^{+} \alpha_{\lambda+q} + A_{\lambda q}^{+} \alpha_{\lambda} \alpha_q \alpha_{\lambda+q}^{+}) \quad (5.5)$$

where

$$A_{\lambda q}^{\pm} = - \frac{1}{2} (2SN^{-1})^{\dagger} (T_{\lambda}^{\pm} + T_q^{\pm}) \quad (5.6)$$

Transition probabilities leading to creation of spin wave with wave vector $\vec{\mu}$ are:

$$W_{(a_{\mu}, a_{\nu}, a_{\sigma}) \rightarrow (a_{\mu}+1, a_{\nu}-1, a_{\sigma}-1)}^{(3)} = (8\pi/\hbar) A_{\nu\sigma}^{+} A_{\nu\sigma}^{-} (a_{\mu}+1) a_{\nu} a_{\sigma} \delta(\varepsilon_{\mu} - \varepsilon_{\nu} - \\ - \varepsilon_{\sigma}) \delta(\vec{\mu} - \vec{\nu} - \vec{\sigma}) \\ W_{(a_{\mu}, a_{\nu}, a_{\sigma}) \rightarrow (a_{\mu}+1, a_{\nu}+1, a_{\sigma}-1)}^{(3)} = (8\pi/\hbar) A_{\mu\nu}^{+} A_{\mu\nu}^{-} (a_{\mu}+1) (a_{\nu}+1) a_{\sigma} \delta(\varepsilon_{\mu} + \\ + \varepsilon_{\nu} - \varepsilon_{\sigma}) \delta(\vec{\mu} + \vec{\nu} - \vec{\sigma}) \\ W_{(a_{\mu}, a_{\nu}, a_{\sigma}) \rightarrow (a_{\mu}+1, a_{\nu}-1, a_{\sigma}+1)}^{(3)} = (8\pi/\hbar) A_{\mu\sigma}^{+} A_{\mu\sigma}^{-} (a_{\mu}+1) a_{\nu} (a_{\sigma}+1) \delta(\varepsilon_{\mu} - \varepsilon_{\nu} + \\ + \varepsilon_{\sigma}) \delta(\vec{\mu} - \vec{\nu} + \vec{\sigma}) \quad (5.7)$$

where ε_{λ} stands for the spin wave energy determined by (3.27) and

$$\delta(\vec{\lambda}) = 1 \text{ for } \vec{\lambda} = 0 \\ = 0 \text{ for } \vec{\lambda} \neq 0 \quad (5.8)$$

Transition probabilities for annihilation of spin wave $\vec{\mu}$ can be easily obtained from (5.7) by suitable interchange of indices, for instance:

$$W_{(a_\mu, a_\nu, a_\sigma) \rightarrow (a_\mu-1, a_\nu+1, a_\sigma+1)}^{(3)} = (8\pi/\hbar) A_{\sigma\nu}^+ A_{\sigma\nu}^- a_\mu (a_\nu + 1) (a_\sigma + 1) \delta(\varepsilon_\mu - \varepsilon_\nu - \varepsilon_\sigma) \delta(\vec{\mu} - \vec{\nu} - \vec{\sigma}) \quad (5.9)$$

b) Transition probabilities for processes with 4 spin waves

$\tilde{\mathcal{H}}_4$ may be written as

$$\tilde{\mathcal{H}}_4 = \sum_{\lambda\sigma\tau} Y_{\tau\sigma}^\lambda \alpha_{\tau-\lambda}^+ \alpha_{\sigma+\lambda}^+ \alpha_\tau \alpha_\sigma \quad (5.10)$$

where (5.11)

$$-4N Y_{\tau\sigma}^\lambda = J(\gamma_\lambda + \gamma_{\tau-\sigma-\lambda} - \gamma_{\tau-\lambda} - \gamma_{\sigma+\lambda}) - (2\Delta_\lambda + 2\Delta_{\tau-\sigma-\lambda} + \Delta_{\tau-\lambda} + \Delta_{\sigma+\lambda})$$

$$\Delta_\lambda = \frac{1}{2} \sum_{h \neq 0} (1 - 3h_x^2/h^2) D(h) \exp(-i\vec{\lambda} \cdot \vec{h}) \quad (5.12)$$

Transition probability per unit of time for creation of spin wave $\vec{\mu}$ is

$$W_{(a_\mu, a_\kappa, a_\nu, a_\sigma) \rightarrow (a_\mu+1, a_\kappa+1, a_\nu-1, a_\sigma-1)}^{(4)} = (8\pi/\hbar) (Y_{\sigma\nu}^{\mu-\nu} + Y_{\sigma\nu}^{\kappa-\nu}) (Y_{\kappa\mu}^{\nu-\mu} + Y_{\kappa\mu}^{\sigma-\nu}) \times$$

$$\times (a_\mu + 1) (a_\kappa + 1) a_\nu a_\sigma \delta(\varepsilon_\mu + \varepsilon_\kappa - \varepsilon_\nu - \varepsilon_\sigma) \delta(\vec{\mu} + \vec{\kappa} - \vec{\nu} - \vec{\sigma}) \quad (5.13)$$

The other two expressions which are to be considered can be found by cyclic interchange of indices.

For annihilation on the spin wave $\vec{\mu}$ we have

$$W_{(a_\mu, a_\kappa, a_\nu, a_\sigma) \rightarrow (a_\mu-1, a_\kappa-1, a_\nu+1, a_\sigma+1)}^{(4)} = (8\pi/\hbar) (Y_{\sigma\nu}^{\mu-\nu} + Y_{\sigma\nu}^{\kappa-\nu}) (Y_{\kappa\mu}^{\nu-\mu} + Y_{\kappa\mu}^{\sigma-\nu}) \times$$

$$\times a_\mu a_\kappa (a_\nu + 1) (a_\sigma + 1) \delta(\varepsilon_\mu + \varepsilon_\kappa - \varepsilon_\nu - \varepsilon_\sigma) \delta(\vec{\mu} + \vec{\kappa} - \vec{\nu} - \vec{\sigma}) \quad (5.14)$$

and other two expressions by interchange of indices.

In order to get the kinetic equation from transition probabilities given above average numbers of transitions must be obtained. The process of averaging transition probabilities over suitable ensemble of systems at given conditions, simple and requiring no comments in the traditional approach, must be discussed in some detail in our case since in this averaging kinematical interactions must be taken into account. We can simplify the discussion by assumption (implicitly involved in already cited papers of Akhieser 1946, Kaganov, Tsukernik 1958) that average of the product of quantities a_λ is approximately equal to the product of averages. This assumption seems to be quite satisfactorily fulfilled because the dynamical interactions between spin waves are weak. The problem is thus reduced to obtaining the average values of a_λ at actual state of the system taking into consideration kinematical interactions.

When the spin wave system is not far from thermodynamical equilibrium it may be assumed (compare for instance Akhieser 1946, Kaganov, Tsukernik 1958) that the average occupation numbers are equal

$$\bar{a}_\lambda = \bar{a}_\lambda^0 + \xi_\lambda \quad (5.15)$$

where \bar{a}_λ^o is the average equilibrium value of a_λ at given temperature of the spin-system and the time dependent part ξ_λ is small compared with \bar{a}_λ^o . In most experimental situations this assumption seems to be well fulfilled excluding only ferromagnetic resonance saturation experiments at high microwave power.

Since, as it shall be evident from calculations given below, the quantities ξ_λ do not enter into the formula for relaxation time, only average values at equilibrium \bar{a}_λ^o must be determined. Fortunately, this intricate problem of evaluating \bar{a}_λ^o when kinematical interactions are taken into account is in principle solved in Dyson's paper (1956 b). Dyson shows namely, that at temperatures low compared with the Curie temperature of ferromagnetic in question, say for $0 < T < \frac{1}{2} T_c$, the contributions from non-physical parts of ideal states to the partition function are negligible. In other words it may be said that in evaluating the partition function of the spin-waves system the restrictions imposed by existence of kinematical interactions are not important. We can thus neglect them in practice. Thus we get for average equilibrium values of occupation numbers \bar{a}_λ^o (neglecting in this point weak dynamical interactions between spin waves) the well known formula:

$$\bar{a}_\lambda^o = (e^{\beta \epsilon_\lambda} - 1)^{-1} \quad (5.16)$$

$$\beta = (kT)^{-1}$$

The mean net rate of change of the number a_μ of spin waves with wave vector $\vec{\mu}$ is calculated as the mean difference between the number of spin waves created as a result of collisions per unit of time and the number of annihilated ones per unit of time. The resulting kinetic equation is:

$$\left(\frac{da_\mu}{dt} \right)_{\text{coll.}} = (8\pi/\hbar) \sum_{\nu\sigma} \{ A_{\nu\sigma}^+ A_{\nu\sigma}^- [(\bar{a}_\mu + 1) \bar{a}_\nu \bar{a}_\sigma - \bar{a}_\mu (\bar{a}_\nu + 1) (\bar{a}_\sigma + 1)] \delta(\epsilon_\mu - \epsilon_\nu - \epsilon_\sigma) \delta(\vec{\mu} - \vec{\nu} - \vec{\sigma}) + 2A_{\mu\nu}^+ A_{\mu\nu}^- [(\bar{a}_\mu + 1) (\bar{a}_\nu + 1) \bar{a}_\sigma - \bar{a}_\mu \bar{a}_\nu (\bar{a}_\sigma + 1)] \delta(\epsilon_\mu + \epsilon_\nu - \epsilon_\sigma) \delta(\vec{\mu} + \vec{\nu} - \vec{\sigma}) \} + (24\pi/\hbar) \sum_{\kappa\nu\sigma} (Y_{\sigma\nu}^{\mu-\nu} + Y_{\sigma\nu}^{\kappa-\nu}) (Y_{\mu\kappa}^{\nu-\sigma} + Y_{\mu\kappa}^{\nu-\kappa}) [(\bar{a}_\mu + 1) (\bar{a}_\kappa + 1) \bar{a}_\nu \bar{a}_\sigma - \bar{a}_\mu \bar{a}_\kappa (\bar{a}_\nu + 1) (\bar{a}_\sigma + 1)] \delta(\epsilon_\mu + \epsilon_\kappa - \epsilon_\nu - \epsilon_\sigma) \delta(\vec{\mu} + \vec{\kappa} - \vec{\nu} - \vec{\sigma}) \quad (5.17)$$

where we have taken into account the symmetry properties of coefficients $Y_{\sigma\nu}^\lambda = Y_{\nu\sigma}^{-\lambda}$

Putting \bar{a}_λ given by (5.15) into the equation (5.17) and — on account of $|\xi_\lambda| \ll \bar{a}_\lambda^o$ — retaining only terms linear in deviations ξ_λ the eq. (5.17) can be reduced to the form

$$\left(\frac{da_\mu}{dt} \right)_{\text{coll.}} = -\frac{1}{\tau_\mu} \xi_\mu - \sum \frac{1}{\tau} \xi \quad (5.18)$$

In deriving this equation the formula (5.16) was taken into account and that thus expressions of the form

$$[(\bar{a}_\mu^o + 1) \bar{a}_\nu^o \bar{a}_\sigma^o - \bar{a}_\mu^o (\bar{a}_\nu^o + 1) (\bar{a}_\sigma^o + 1)] \delta(\epsilon_\mu - \epsilon_\nu - \epsilon_\sigma) = 0 \quad (5.19)$$

vanish.

Equation (5.18) defines relaxation time $\tau_{\vec{\mu}}$ for spin waves $\vec{\mu}$, $(\tau_{\vec{\mu}})^{-1}$ is thus given by:

$$\begin{aligned}
 (\tau_{\vec{\mu}})^{-1} = & (8\pi/\hbar) \sum_{\nu\sigma} \{A_{\nu\sigma}^+ A_{\nu\sigma}^- (\bar{a}_{\nu}^{\circ} + \bar{a}_{\sigma}^{\circ} + 1) \delta(\varepsilon_{\mu} - \varepsilon_{\nu} - \varepsilon_{\sigma}) \delta(\vec{\mu} - \vec{\nu} - \vec{\sigma}) + \\
 & + 2A_{\mu\nu}^+ A_{\mu\nu}^- (\bar{a}_{\sigma}^{\circ} - \bar{a}_{\nu}^{\circ}) \delta(\varepsilon_{\mu} + \varepsilon_{\nu} - \varepsilon_{\sigma}) \delta(\vec{\mu} + \vec{\nu} - \vec{\sigma})\} + \\
 & + (24\pi/\hbar) \sum_{\kappa\nu\sigma} (Y_{\sigma\nu}^{\mu-\nu} + Y_{\sigma\nu}^{\kappa-\nu}) (Y_{\mu\kappa}^{\mu-\nu} + Y_{\mu\kappa}^{\nu-\kappa}) [\bar{a}_{\kappa}^{\circ} (\bar{a}_{\nu}^{\circ} + \bar{a}_{\sigma}^{\circ} + 1) - \\
 & - \bar{a}_{\nu}^{\circ} \bar{a}_{\sigma}^{\circ}] \delta(\varepsilon_{\mu} + \varepsilon_{\kappa} - \varepsilon_{\nu} - \varepsilon_{\sigma}) \delta(\vec{\mu} + \vec{\kappa} - \vec{\nu} - \vec{\sigma}) \quad (5.20)
 \end{aligned}$$

This equation forms the basis for calculation of relaxation time. A case important for practical purposes is discussed in § 6.

§ 6. Relaxation time for spin waves with zero wave vector

As a simple application of the above consideration we will discuss practically important case i. e. relaxation of spin waves with wave vector $\vec{\mu} = 0$, which are first of all excited in conditions of microwave resonance absorption experiments. It is expected (Kasuya 1954, V. Kranendonk, V. Vleck 1958) that as a result of several mechanisms spin waves with nonzero wave vectors may be also excited in ferromagnetic resonance. More detailed analysis of this question will be given in subsequent paper.

As usual the analysis will be limited to long spin waves only, i. e. we assume $\vec{\delta} \cdot \vec{\lambda} \ll 1$ where $\vec{\delta}$ is a vector between neighbouring lattice points. In this approximation the energy of spin waves takes the well known quadratic character:

$$\begin{aligned}
 \varepsilon_{\lambda} & \approx L + \omega \lambda^2 \\
 \omega & = JSa^2 \quad (6.1)
 \end{aligned}$$

(a is the lattice constant).

It is evident, that for spin wave $\vec{\mu} = 0$ transition probabilities (5.7) for 3-wave processes are vanishing, as the momentum and energy conservation laws (expressed by δ -factors) cannot be fulfilled. Only 4-wave processes have to be discussed.

For pseudo-dipolar interactions coefficient Δ_{λ} (5.12) may be evaluated in nearest neighbour approximation with coupling constant D . The result for long spin waves is

$$\Delta_{\lambda} \approx -p (\lambda^2 - 3\lambda_x^2) \quad (6.2)$$

with

$$\begin{aligned}
 p_c &= \frac{1}{2} Da^2 && \text{for simple cubic lattice} \\
 p_{bcc} &= 0 && \text{for body centered cubic lattice} \\
 p_{fcc} &= \frac{1}{8} Da^2 && \text{for face centered cubic lattice}
 \end{aligned} \quad (6.3)$$

Inverse relaxation time is thus obtained from eq. (5.20) for waves with $\vec{\mu} = 0$

$$\begin{aligned} \tau_o^{-1} = & (27\pi p^2 / \hbar \omega N^2) \sum_{\kappa \nu \sigma} [\nu^2 + \sigma^2 - 3(\nu_z^2 + \sigma_z^2) - 2\nu_z \sigma_z] \\ & \times [\nu^2 + \sigma^2 - 3(\nu_z^2 + \sigma_z^2)] [\bar{a}_\kappa^o (\bar{a}_\nu^o + \bar{a}_\sigma^o + 1) - \bar{a}_\nu^o \bar{a}_\sigma^o] \\ & \times \delta(\vec{\nu} \cdot \vec{\sigma}) \delta(\vec{\kappa} - \vec{\nu} - \vec{\sigma}) \end{aligned} \quad (6.4)$$

The sums can be evaluated by transforming them into integrals in the usual way:

$$\sum (...) = N (a^3/n) (2\pi)^{-3} \int d\vec{\nu} (...) \quad (6.5)$$

where the numerical factor n equals 1, 2, 4 for simple cubic, body centered cubic and face centered cubic lattice respectively. As the main contributions to sums in (6.4) come from small values of wave vectors the integrals may be extended to the whole reciprocal lattice rather than confined to the first Brillouin zone only. Introducing polar coordinates, integrating over polar angles and passing to new integration variables:

$$x = \beta \omega \sigma^2$$

$$y = \beta \omega \nu^2$$

we get finally:

$$\begin{aligned} \tau_o^{-1} = & \frac{3^3}{20(2\pi)^3} r^2 \left(\frac{D}{J} \right)^2 \frac{J}{\hbar S} \left(\frac{kT}{JS} \right)^4 \int_0^\infty dx \int_0^\infty dy (x^2 - xy + y^2) \\ & \times \left[\frac{1}{e^{\varepsilon+x+y} - 1} \left(\frac{1}{e^{\varepsilon+x} - 1} + \frac{1}{e^{\varepsilon+y} - 1} + 1 \right) - \frac{1}{e^{\varepsilon+x} - 1} \frac{1}{e^{\varepsilon+y} - 1} \right] \end{aligned} \quad (6.6)$$

wherein:

$$\varepsilon = \beta L = 2\mu_B H/kT \quad (6.7)$$

and r equals 1, 0, 2^{-4} for the simple, body centered, and face centered lattices, respectively.

In the case $\varepsilon \ll 1$ (for weak magnetic fields and not very low temperatures) the inverse relaxation time varies approximately as T^4 . For very low temperatures $\varepsilon \gg 1$ and τ_o^{-1} is proportional to $T^4 \exp(-2\mu_B H/kT)$, rapidly tending to zero as the temperature tends to zero.

As an example the numerical values for nickel may be given.

For Ni:

$$r_{fcc} = 2^{-4}$$

$$S = \frac{1}{2}$$

$J \cong 2 \cdot 230 k \cdot 1^0 K$ (see Kittel, 1954); the factor 2 appears owing to different definitions of exchange integral in Kittel's book and in the present paper. For $\varepsilon \ll 1$ we get

$$\tau_o^{-1} \cong 1.8 \times 10^9 \cdot (D/J)^2 (T/230^\circ)^4 \quad (6.8)$$

The ratio of pseudo-dipolar coupling constant D to the exchange integral J is very difficult to estimate. As a first, very rough estimation it may be taken as (Van Vleck 1956)

$$D/J \sim (g - 2)^2$$

where g is an experimental value of the spectroscopic splitting factor. From ferromagnetic resonance measurements it follows (Kittel 1954)

$$g \cong 2.2$$

and so from (6.8)

$$\tau_0^{-1} \sim 10^6 (T/230^\circ)^4 \text{ sec}^{-1} \quad (6.9)$$

The order of magnitude of the relaxation time indicates that the processes considered here cannot determine the line width of ferromagnetic resonance.

Comparing our result with the results obtained by Kasuya (1954 a) on the basis of Holstein—Primakoff's theory we may remark that: 1) in our considerations exchange forces do not contribute to relaxation of spin waves with zero wave vector, 2) the relaxation time varies in our case as T^{-4} (for not very low temperature) while Kasuya found T^{-3} . For nickel the value of τ_0 at room temperature obtained from (6.9) is several times shorter than value which may be deduced from formula (3) of Kasuya's paper (1954 a).

To complete the considerations presented here relaxation time of spin waves with nonzero wave vectors must be calculated. This will be done in the second part of this paper.

I wish to thank Professor S. Szczeniowski for encouragement and valuable discussions.

Appendix 1.

It may be shown that omitting of the terms

$$\sum_{\lambda} (Q_{\lambda}^{+} \alpha_{\lambda}^{+} \alpha_{-\lambda}^{+} + Q_{\lambda}^{-} \alpha_{\lambda} \alpha_{-\lambda}) \quad (\text{A I.1})$$

in $\tilde{\mathcal{H}}_0$ of eq. (3.26) is equivalent to the neglect of quantities of the order of $(D/J)^2$ as compared to unity (in connection with this section compare Akhiezer 1946). By means of Holstein — Primakoff's (1940, eqs. (16)—(18)) transformation

$$\begin{aligned} \alpha_{\lambda} &= 2^{-\frac{1}{2}} e^{i\varphi_{\lambda}} (b_{\lambda} + b_{-\lambda}) \\ \alpha_{-\lambda} &= 2^{-\frac{1}{2}} e^{i\varphi_{-\lambda}} (b_{\lambda} - b_{-\lambda}) \\ b_{\lambda} &= l_1 c_{\lambda} + l_2 c_{\lambda}^{+} \\ b_{-\lambda} &= l_1 c_{-\lambda} - l_2 c_{-\lambda}^{+} \end{aligned} \quad (\text{A I.2})$$

where φ_λ is polar angle of the vector $\vec{\lambda}$,

$$l_1 = \left\{ \frac{1}{2} \frac{\varepsilon_\lambda + (\varepsilon_\lambda^2 - |2Q_\lambda|^2)^{1/2}}{(\varepsilon_\lambda - |2Q_\lambda|^2)^{1/2}} \right\}^{1/2} \quad (\text{A I.3})$$

and

$$l_2 = \left\{ \frac{1}{2} \frac{\varepsilon_\lambda - (\varepsilon_\lambda^2 - |2Q_\lambda|^2)^{1/2}}{(\varepsilon_\lambda^2 - |2Q_\lambda|^2)^{1/2}} \right\}^{1/2}$$

$$|Q_\lambda| = |Q_\lambda^\pm|$$

$\tilde{\mathcal{H}}_0$ of eq. (3.26) may be diagonalized

$$\tilde{\mathcal{H}}_0 = \sum_\lambda (\varepsilon_\lambda^2 - |2Q_\lambda|^2)^{1/2} c_\lambda^\dagger c_\lambda \quad (\text{A I.4})$$

and interaction Hamiltonian $\tilde{\mathcal{H}}_I$ expressed in terms of operators $c_\lambda^\dagger, c_\lambda$. In the nearest neighbours approximation and for long waves the ratio:

$$|2Q_\lambda|/\varepsilon_\lambda \sim D/J \quad (\text{A I.5})$$

is small as compared to 1. Thus approximately, with error of order $(D/J)^2$

$$(\varepsilon_\lambda^2 - |2Q_\lambda|^2)^{1/2} \cong \varepsilon_\lambda \quad (\text{A I.6})$$

$$l_1 \cong 1 \quad l_2 \cong 0$$

and (A I.4) reduces to:

$$\tilde{\mathcal{H}}_0 \cong \sum_\lambda \varepsilon_\lambda c_\lambda^\dagger c_\lambda \quad (\text{A I.4'})$$

Returning to the old operators $a_\lambda^\dagger, a_\lambda$ eq. (A I.4') is replaced by:

$$\tilde{\mathcal{H}}_0 \cong \sum_\lambda \varepsilon_\lambda a_\lambda^\dagger a_\lambda \quad (\text{A I.7})$$

and interaction Hamiltonian takes the primary form determined by eqs (3.22)—(3.26). It is thus proved that omission of operator (A I.1) is equivalent to approximation (A I.6), connected with rather small error as the condition $(D/J)^2 \ll 1$ is in practice well fulfilled.

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ÜBER EINE EXPERIMENTELLE METHODE ZUR UNTERSCHIEDUNG DER VERSCHIEDENEN ARTEN DER MULTIPOLSTRAHLUNG IM RÖNTGENSPEKTRUM

I. VERALLGEMEINERUNG DES REZIPROZITÄTSTHEOREMS FÜR ELEKTROMAGNETISCHE MULTIPOLSTRAHLUNGSQUELLEN

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Das von H. A. Lorentz im Jahre 1896 für die elektrische und magnetische Dipolstrahlung angegebene elektromagnetische Reziprozitätstheorem wird für elektrische und magnetische Multipolstrahlungen beliebiger Ordnung verallgemeinert. Für den Fall der elektrischen und magnetischen Dipol- sowie der elektrischen Quadrupolstrahlung werden Formeln angegeben, die die im verallgemeinerten Reziprozitätstheorem auftretenden Entwicklungskoeffizienten durch die elektromagnetischen Feldstärken und ihre Ableitungen ausdrücken. Das Theorem ist sowohl zur Lösung technischer Probleme (Ausbreitung von Radiowellen von Antennen endlicher Größe und beliebiger Gestalt) als auch physikalischer Probleme (Bestimmung der Art der Multipolquellen im Gebiet der Röntgenstrahlung; Lösung exakter elektromagnetischer Beugungsprobleme für beliebige Multipolquellen, wenn solche für elektrische und magnetische Dipolquellen bekannt sind) verwendbar.

Die Frage, welcher elektrischen oder magnetischen Multipolstrahlung eine Spektrallinie ihre Entstehung verdankt, kann im optischen Wellenlängenbereich experimentell mit Hilfe des Zeemaneffektes entschieden werden. Im Gebiete der Röntgenstrahlung versagt dieses Hilfsmittel jedoch vollkommen. Und gerade hier wäre es interessant eine Methode zur Ermittlung des Multipolcharakters der Spektrallinien zu besitzen, da ja im Röntgenspektrum mit wachsender Atomzahl die Strahlung der höheren Multipole gegenüber der elektrischen Dipolstrahlung immer mehr hervortritt. Bei Uran beträgt z. B. die Intensität der elektrischen Quadrupollinien bereits ungefähr $1/10$ der stärksten elektrischen Dipollinien (Rubinowicz-Blaton 1932).

Eine andere Methode zur experimentellen Ermittlung des Multipolcharakters der elektromagnetischen Strahlung bieten die Weitwinkelinterferenzen. Bereits im

Jahre 1911 hat P. Selényi (1911) gezeigt, daß sie zum Nachweis der elektrischen Dipolstrahlung im optischen Wellenlängengebiet verwendet werden können. Aber auch in dem uns interessierenden Röntgenstrahlengebiet treten sie in Erscheinung, nämlich bei den Kosselschen Versuchen (Kossel, Loeck und Voges 1935, Kossel 1937) mit Röntgeninterferenzen an Gitterquellen in Kristallen. Ich habe daher schon vor einigen Jahren (Rubinowicz 1949) darauf aufmerksam gemacht, daß diese Interferenzerscheinungen zur experimentellen Ermittlung des Multipolcharakters der Röntgenstrahlung der Atome benützt werden könnten. Dazu wäre nur die experimentelle Bestimmung der relativen Intensitäten der Kosselschen Beugungsstreifen erforderlich. Allerdings ist die in Rede stehende Erscheinung sehr lichtschwach und wurde auf photographischem Wege bisher nur bei den stärksten elektrischen Dipollinien (K_α und K_β) beobachtet. Da jedoch die begründete Aussicht besteht, daß zur Beobachtung der Kosselschen „vollständigen Reflexsysteme“ die ungleich empfindlicheren und für Intensitätsmessungen sehr bequemen Photoelektronenvervielfacher verwendet werden können, glaube ich daß es bereits an der Zeit ist, eine entsprechende Theorie für die elektrischen Quadrupol-Röntgenlinien zu entwickeln. Dies ist umso notwendiger, als diese Erscheinung wenigstens gegenwärtig unsere einzige Hoffnung ist, auf experimentellem Wege den Multipolcharakter der Röntgenstrahlung der Atome und eventuell auch der hinreichend weichen γ -Strahlung radioaktiver Kerne zu bestimmen. Allerdings muß bemerkt werden, daß selbst bei den elektrischen Dipollinien einige wenige experimentelle Einzelheiten noch nicht vollständig geklärt sind (vgl. Kossel 1937, v. Laue 1937, 1941, 1948). M. v. Laue (1937, 1941, 1948) ist jedoch der Ansicht, daß eine bessere Näherung seiner dynamischen Theorie der Röntgeninterferenzen zu einem Verständnis der bisher ungeklärten Einzelheiten führen muß.

In der vorliegenden Abhandlung soll eine Vorarbeit zur Inangriffnahme des oben formulierten Problems erledigt werden. Max von Laue (1935, 1937, 1941, 1948) hat bei der elektrischen Dipolstrahlung einen sehr eleganten Weg eingeschlagen, der auf der Verwendung des Reziprozitätstheorems¹ für die elektrische Dipolstrahlung beruht. Auch in dem Falle der elektrischen Quadrupolstrahlung ist dieser Weg gangbar, wenn nur das Reziprozitätstheorem entsprechend verallgemeinert wird. Eine solche Verallgemeinerung und zwar sogleich für die elektrischen und magnetischen Multipolstrahlungen beliebiger Ordnungen sollen die nachstehenden Betrachtungen liefern. Sie scheint mir nämlich auch für andere physikalische und technische Probleme, bei denen Multipolstrahlungen auftreten, von Interesse zu sein.

In der Physik kann man z. B. aus den strengen Lösungen der Beugungsprobleme für beliebig im Raume orientierte elektrische und magnetische Dipole exakte Lösungen der gleichen Probleme für beliebige elektrische und magnetische Multipolquellen herstellen.

¹ Der erste Beweis für das elektromagnetische Reziprozitätstheorem für die elektrische und magnetische Dipolstrahlung rührt wohl von H. A. Lorentz (1896) her (vgl. dazu Rubinowicz 1957, S. 242). Für diese beiden Fälle hat auch Sommerfeld (1931) einen Beweis angegeben.

Als ein technisches Problem sei das Problem der Ausbreitung der Radiowellen genannt, die von einer Antenne endlicher Größe und beliebiger Gestalt emittiert werden. Die Strahlung einer solchen Antenne kann man nämlich durch eine geeignete Superposition von elektrischen und magnetischen Multipolstrahlungen erhalten. Da man mit Hilfe des Reziprozitätstheorems elektromagnetische Felder höherer Multipolquellen aus denen einer elektrischen und einer magnetischen Dipolquelle erhalten kann, ist somit grundsätzlich die Lösung des Problems der Strahlung einer beliebigen Antenne aus der Lösung des gleichen Problems für Dipolantennen ableitbar und zwar sowohl im Falle der ebenen als auch der kugelförmigen Erde.

Falls es künftig gelingen sollte, die Kosselschen Röntgeninterferenzen zu beobachten, die von der γ -Strahlung radioaktiver Kerne erzeugt werden, könnte man das in der vorliegenden Arbeit angegebene Reziprozitätstheorem zur Berechnung der für die einzelnen Multipolstrahlungen höherer Ordnung charakteristischen Intensitäten der Kosselschen Interferenzstreifen verwenden.

§ 1. Der Integralsatz von H. A. Lorentz

Im folgenden betrachten wir ausschließlich zeitlich harmonisch-periodische elektromagnetische Felder, deren Zeitfaktor durch $e^{-i\omega t}$ gegeben wird. Wir nehmen an, daß zwei solche Felder vorhanden sind, deren komplexe Feldstärken wir bis auf den Zeitfaktor mit $\mathbf{E}_1, \mathbf{H}_1$ und $\mathbf{E}_2, \mathbf{H}_2$ bezeichnen. Setzen wir voraus, daß keine räumlichen Ströme vorhanden sind, so erfüllen diese Feldstärken die Maxwellschen Gleichungen

$$-i\kappa_s \mathbf{E} = \text{rot } \mathbf{H}, \quad i\kappa_\mu \mathbf{H} = \text{rot } \mathbf{E}, \quad (1.1)$$

wobei

$$\kappa_s = \frac{\varepsilon\omega}{c}, \quad \kappa_\mu = \frac{\mu\omega}{c}. \quad (1.2)$$

Bezeichnen wir durch einen Stern den konjugiert-komplexen Wert eines Vektors, so folgt aus der identischen Vektorrelation

$$\text{div} (\mathbf{E}_1 \times \mathbf{H}_2^* + \mathbf{E}_2^* \times \mathbf{H}_1) = \mathbf{H}_2^* \text{ rot } \mathbf{E}_1 - \mathbf{E}_1 \text{ rot } \mathbf{H}_2^* + \mathbf{H}_1 \text{ rot } \mathbf{E}_2^* - \mathbf{E}_2^* \text{ rot } \mathbf{H}_1$$

mit Rücksicht auf die Maxwellschen Gleichungen (1.1) die Beziehung

$$\text{div} (\mathbf{E}_1 \times \mathbf{H}_2^* + \mathbf{E}_2^* \times \mathbf{H}_1) = 0.$$

Integrieren wir sie über einen durch die Fläche F begrenzten Raum R , so erhalten wir mit Hilfe des Gaußschen Satzes den zuerst von H. A. Lorentz (1896) angegebenen Integralsatz

$$\int_F [(\mathbf{E}_1 \times \mathbf{H}_2^*)_n + (\mathbf{E}_2^* \times \mathbf{H}_1)_n] df = 0 \quad (1.3)$$

und zwar in der Gestalt, in der wir ihn weiter unten verwenden werden. Wir setzen dabei voraus, daß n die äußere Normale an die Begrenzungsfläche F bedeutet. Innerhalb des Raumes R müssen die Felder $\mathbf{E}_1, \mathbf{H}_1$ und $\mathbf{E}_2, \mathbf{H}_2$ im allgemeinen regulär sein. Gleichung (1.3) gilt aber auch, falls Sprungflächen von ε und μ auftreten, wenn nur in diesen Flächen die Tangentialkomponenten der elektromagnetischen Feldstärken stetig sind. Ebenso gilt (1.3) wenn im Raume R irgend welche vollkommenen Leiter vorgegeben sind, da an ihren Begrenzungsflächen die Tangentialkomponenten der elektrischen Feldstärke verschwinden.

Wenn das Raumgebiet R nach allen Richtungen hin sich gleichmäßig ins Unendliche erstreckt, so ist es nicht notwendig in (1.3) auch den Beitrag der im Unendlichen liegenden Begrenzungsfläche F_∞ zu berücksichtigen, falls nur beide elektromagnetischen Felder im Unendlichen die Sommerfeldsche Endlichkeitsbedingung erfüllen und ferner das eine von ihnen, etwa $\mathbf{E}_1, \mathbf{H}_1$, hier der Sommerfeldschen Ausstrahlungs- und das andere $\mathbf{E}_2, \mathbf{H}_2$ der Einstrahlungsbedingung genügt. Überdies muß auch noch vorausgesetzt werden, daß die unendlich ferne Fläche F_∞ in der Weise entsteht, daß eine im Endlichen liegende Fläche F gleichmäßig nach allen Richtungen hin ins Unendliche verlagert wird. Wir können daher F_∞ als eine Kugelfläche ansehen.

Bezeichnet \mathbf{r} den Radiusvektor mit einem Anfangspunkt im Endlichen, und \mathbf{r}_0 den zugehörigen Einheitsvektor, so verlangt die Endlichkeitsbedingung daß

$$\lim_{r \rightarrow \infty} r \mathbf{E} = \text{endlich}, \quad (1.4a)$$

$$\lim_{r \rightarrow \infty} r \mathbf{H} = \text{endlich} \quad (1.4b)$$

ist. Die Ausstrahlungsbedingung¹ fordert hingegen, daß

$$\lim_{r \rightarrow \infty} r \left(\sqrt{\frac{\varepsilon}{\mu}} \mathbf{E} + \mathbf{r}_0 \times \mathbf{H} \right) = 0, \quad (1.5a)$$

$$\lim_{r \rightarrow \infty} r \left(\sqrt{\frac{\mu}{\varepsilon}} \mathbf{H} - \mathbf{r}_0 \times \mathbf{E} \right) = 0 \quad (1.5b)$$

und die Einstrahlungsbedingung daß

$$\lim_{r \rightarrow \infty} r \left(\sqrt{\frac{\varepsilon}{\mu}} \mathbf{E} - \mathbf{r}_0 \times \mathbf{H} \right) = 0, \quad (1.6a)$$

$$\lim_{r \rightarrow \infty} r \left(\sqrt{\frac{\mu}{\varepsilon}} \mathbf{H} + \mathbf{r}_0 \times \mathbf{E} \right) = 0. \quad (1.6b)$$

Um zu zeigen, daß der Beitrag von F_∞ verschwindet, bemerken wir zunächst daß $\mathbf{E}_2^*, \mathbf{H}_2^*$ zugleich mit $\mathbf{E}_2, \mathbf{H}_2$ die Endlichkeitsbedingung (1.4) sowie die Einstrah-

¹ Bezüglich der Literaturangaben und der physikalischen Bedeutung der beiden Bedingungen (1.4) und (1.5) vgl. etwa Rubinowicz (1957).

lingsbedingung (1.6) erfüllt. Aus der Endlichkeitsbedingung (1.4a) für \mathbf{E}_1 und der Einstrahlungsbedingung (1.6b) für \mathbf{E}_2^* , \mathbf{H}_2^* folgt sodann die Beziehung

$$\lim_{r \rightarrow \infty} r^2 \left[\sqrt{\frac{\mu}{\varepsilon}} (\mathbf{E}_1 \times \mathbf{H}_2^*) + \mathbf{E}_1 \times (\mathbf{r}_0 \times \mathbf{E}_2^*) \right] = 0 \quad (1.7)$$

und aus der Endlichkeitsbedingung (1.4a) für \mathbf{E}_2^* und der Ausstrahlungsbedingung (1.5b) für \mathbf{E}_1 , \mathbf{H}_1 die Beziehung

$$\lim_{r \rightarrow \infty} r^2 \left[\sqrt{\frac{\mu}{\varepsilon}} (\mathbf{E}_2^* \times \mathbf{H}_1) - \mathbf{E}_2^* \times (\mathbf{r}_0 \times \mathbf{E}_1) \right] = 0. \quad (1.8)$$

Auf F_∞ ist nun $df = r^2 d\omega$, wenn $d\omega$ ein Flächenelement der Einheitskugel um den Anfangspunkt des Vektors \mathbf{r} bezeichnet. Da auf F_∞ die Richtungen von \mathbf{r}_0 und \mathbf{n} zusammenfallen, so ergibt die skalare Multiplikation von (1.7) und (1.8) mit dem Vektor der Normalen \mathbf{n} im Einklang mit unserer Behauptung das Verschwinden des Flächenintegrals, das in der Lorentzschen Beziehung (1.3) über die Fläche F_∞ zu erstrecken ist.

In der Fassung (1.3), die wir dem Beweis des Reziprozitätstheorems zugrunde legen, stellt der Lorentzsche Integralsatz eine Beziehung dar, zwischen den komplexen Feldstärken \mathbf{E}_1 , \mathbf{H}_1 des einen Feldes und den konjugiert-komplexen Werten \mathbf{E}_2^* , \mathbf{H}_2^* der komplexen Feldstärken eines zweiten Feldes \mathbf{E}_2 , \mathbf{H}_2 . Man kann jedoch den Lorentzschen Integralsatz auch in der Gestalt

$$\int_F [(\mathbf{E}_1 \times \mathbf{H}_2)_n - (\mathbf{E}_2 \times \mathbf{H}_1)_n] df = 0 \quad (1.9)$$

verwenden, in der direkt die beiden komplexen Feldstärken \mathbf{E}_1 , \mathbf{H}_1 und \mathbf{E}_2 , \mathbf{H}_2 auftreten. Damit der Beitrag der unendlich fernen Fläche F_∞ zum Integralsatz (1.9) verschwindet, muß man jedoch fordern, daß die Felder \mathbf{E}_1 , \mathbf{H}_1 und \mathbf{E}_2 , \mathbf{H}_2 im Unendlichen außer der Endlichkeitsbedingung (1.4) beide zugleich entweder die Ausstrahlungs- oder die Endlichkeitsbedingung (1.5) bzw. (1.6) erfüllen. Die Fassung (1.9) des Lorentzschen Integralsatzes ergibt (vgl. das verallgemeinerte Reziprozitätstheorem für den Fall der skalaren Wellengleichung, Rubinowicz 1955) ein Reziprozitätstheorem, das ganz ebenso wie (3.16) gebaut ist, in dem jedoch in den Produkten der Koeffizienten A_{lm} und a_{lm} die Indizes m entgegengesetzte Vorzeichen haben.

§ 2. Entwicklung eines elektromagnetischen Feldes nach Multipolfeldern

Verwenden wir sphärische Polarkoordinaten r , ϑ , φ und setzen $k^2 = \kappa_e \kappa_\mu$, so stellen nach P. Debye (1908, 1909) \mathbf{E}^{el} , \mathbf{H}^{el} und \mathbf{E}^{mg} , \mathbf{H}^{mg} :

$$\mathbf{E}_r^{el} = \frac{\partial^2 r \Pi^{el}}{\partial r^2} + k^2 r \Pi^{el}, \quad \mathbf{E}_r^{mg} = 0,$$

$$E_{\theta}^{el} = \frac{1}{r} \frac{\partial^2 r \Pi^{el}}{\partial \vartheta \partial r},$$

$$E_{\varphi}^{el} = \frac{1}{r \sin \vartheta} \frac{\partial^2 r \Pi^{el}}{\partial \varphi \partial r},$$

(2.1a)

$$H_r^{el} = 0,$$

$$H_{\theta}^{el} = -i \kappa_e \frac{1}{r \sin \vartheta} \frac{\partial r \Pi^{el}}{\partial \varphi},$$

$$H_{\varphi}^{el} = i \kappa_e \frac{1}{r} \frac{\partial r \Pi^{el}}{\partial \vartheta},$$

$$E_{\theta}^{mg} = i \kappa_{\mu} \frac{1}{r \sin \vartheta} \frac{\partial r \Pi^{mg}}{\partial \varphi},$$

$$E_{\varphi}^{mg} = -i \kappa_{\mu} \frac{1}{r} \frac{\partial r \Pi^{mg}}{\partial \vartheta},$$

(2.1b)

$$H_r^{mg} = \frac{\partial^2 r \Pi^{mg}}{\partial r^2} + k^2 r \Pi^{mg},$$

$$H_{\theta}^{mg} = \frac{1}{r} \frac{\partial^2 r \Pi^{mg}}{\partial \vartheta \partial r},$$

$$H_{\varphi}^{mg} = \frac{1}{r \sin \vartheta} \frac{\partial^2 r \Pi^{mg}}{\partial \varphi \partial r}$$

zwei zeitlich harmonisch-periodische Lösungen der Maxwellschen Gleichungen (1.1) dar, falls die Potentiale Π^{el} und Π^{mg} der räumlichen Schwingungsgleichung $\Delta \Pi + k^2 \Pi = 0$ genügen.

Diese Lösungen können auch durch die Vektorrelationen

$$\mathbf{E}^{el} = \text{grad} \frac{\partial r \Pi^{el}}{\partial r} + k^2 \mathbf{r} \Pi^{el},$$

(2.2a)

$$\mathbf{E}^{mg} = -i \kappa_{\mu} \mathbf{r} \times \text{grad} \Pi^{mg},$$

(2.2b)

$$\mathbf{H}^{el} = i \kappa_e \mathbf{r} \times \text{grad} \Pi^{el},$$

$$\mathbf{H}^{mg} = \text{grad} \frac{\partial r \Pi^{mg}}{\partial r} + k^2 \mathbf{r} \Pi^{mg}$$

ausgedrückt werden.

Wir erhalten die elektrische bzw. die magnetische Multipolstrahlung eines 2^l-Pols¹, die einer auslaufenden elektromagnetischen Welle entspricht, also der Sommerfeldschen Ausstrahlungsbedingung (1.5) genügt, falls wir in (2.1) oder (2.2) Π^{el} bzw., Π^{mg} gleich

$$\frac{\eta_l(\varrho)}{\varrho} Y_{lm}(\vartheta, \varphi) \quad (2.3)$$

setzen. Hier bedeutet $Y_{lm}(\vartheta, \varphi)$ die Kugelfunktion

$$Y_{lm}(\vartheta, \varphi) = e^{im\varphi} P_l^m(\cos \vartheta) \quad (2.4)$$

und $\eta_l(\varrho)$ eine Funktion, die sich durch die Hankelsche Funktion $H^{(1)}(\varrho)$ in der nachstehenden Weise ausdrückt:

$$\begin{aligned} \eta_l(\varrho) &= \varrho^{l+1} \left(-\frac{1}{\varrho} \frac{d}{d\varrho} \right)^l - i \frac{e^{i\varphi}}{\varrho} = \left(\frac{\pi \varrho}{2} \right)^{\frac{1}{2}} H_{l+\frac{1}{2}}^{(1)}(\varrho) \\ &= e^{-i\frac{\pi}{2}(l+1)} e^{i\varphi} \left[1 + \frac{i}{2\varrho} \frac{l(l+1)}{1!} - \frac{1}{(2\varrho)^2} \frac{(l-1)l(l+1)(l+2)}{2!} - + + \dots \right]. \end{aligned} \quad (2.5)$$

Dabei ist $\varrho = kr$.

¹ $l = 1, 2, 3, \dots$ entspricht somit einer Dipol-, Quadrupol-, Oktupol- u. s. f. -Strahlung.

Eine einlaufende, also der Sommerfeldschen Einstrahlungsbedingung (1.6) entsprechende elektrische bzw. magnetische Multipolstrahlung eines 2^l -Pols ergibt sich hingegen, wenn wir in (2.3) die Funktion $\eta_l(\varrho)$ durch die gewöhnlich mit $\zeta_l(\varrho)$ bezeichnete Funktion ersetzen. Sie wird für reelle ϱ -Werte durch den konjugiert-komplexen Wert von $\eta_l(\varrho)$ gegeben und ist durch die Hankelsche Funktion $H_{l+\frac{1}{2}}^{(2)}(\varrho)$ in der Gestalt

$$\begin{aligned} \zeta_l(\varrho) &= \varrho^{l+1} \left(-\frac{1}{\varrho} \frac{d}{d\varrho} \right)^l i \frac{e^{-i\varrho}}{\varrho} = \left(\frac{\pi\varrho}{2} \right)^{\frac{1}{2}} H_{l+\frac{1}{2}}^{(2)}(\varrho) \\ &= e^{i\frac{\pi}{2}(l+1)} e^{-i\varrho} \left[1 - \frac{i}{2\varrho} \frac{l(l+1)}{1!} - \frac{1}{(2\varrho)^2} \frac{(l-1)l(l+1)(l+2)}{2!} + + \dots \right] \end{aligned} \quad (2.6)$$

darstellbar.

Das dem Potential (2.3) mit $\eta_l(\varrho)$ oder $\zeta_l(\varrho)$ entsprechende elektromagnetische Feld wird im Koordinatenursprung d. h. für $\varrho = 0$ unendlich. Ein elektromagnetisches Feld, das die gleichen Symmetrieeigenschaften um den Koordinatenursprung aufweist, jedoch hier endlich bleibt, wird erhalten, wenn wir in (2.3) $\eta_l(\varrho)$ durch

$$\begin{aligned} \psi_l(\varrho) &= \left(\frac{\pi\varrho}{2} \right)^{\frac{1}{2}} J_{l+\frac{1}{2}}(\varrho) \\ &= \frac{\varrho^{l+1}}{1 \cdot 3 \dots (2l+1)} \left[1 - \frac{1}{1!} \frac{2l+3}{2} \left(\frac{\varrho}{2} \right)^2 + \frac{1}{2!} \frac{2l+3}{2} \frac{2l+5}{2} \left(\frac{\varrho}{2} \right)^4 - + \dots \right] \end{aligned} \quad (2.7)$$

ersetzen, also aus dem Potential

$$\frac{\psi_l(\varrho)}{\varrho} Y_{lm}(\vartheta, \varphi).$$

$J_{l+\frac{1}{2}}(\varrho)$ bezeichnet hier eine Besselsche Funktion.

Jedes zeitlich harmonisch-periodische elektromagnetische Feld kann durch Superposition der angeführten speziellen elektromagnetischen Felder (2.1a) und (2.1b) oder (2.2a) und (2.2b) dargestellt werden. Der Konvergenzbereich einer solchen Darstellung wird von der Lage der Quellpunkte und der Sprung- und Begrenzungsflächen in dem Raume abhängen, in dem das elektromagnetische Feld gegeben ist.

Im folgenden betrachten wir ausschließlich solche speziellen elektromagnetischen Felder, die nur in einem einzigen Raumpunkte Q eine durch Übereinanderlagerung verschiedener elektrischer und magnetischer Multipole entstehende Strahlungsquelle besitzen. Bezeichnen wir mit $\Pi^{el}(Q, P)$ bzw. $\Pi^{el}(Q, Q)$ die Entwicklung, des zu einem solchen elektromagnetischen Felde gehörigen Π^{el} in der Umgebung eines vom Quellpunkte Q verschiedenen Raumpunktes P bzw. in der Umgebung von Q selbst, so erhalten wir im Falle aus dem Quellpunkt auslaufender

Wellen offensichtlich

$$\Pi^{el}(Q, P) = \sum_{l=0}^{\infty} \sum_{m=-l}^l a_{lm}^{el}(Q, P) \frac{\psi_l(\varrho)}{\varrho} Y_{lm}(\vartheta, \varphi), \quad (2.8a)$$

$$\Pi^{el}(Q, Q) = \sum_{l=0}^{\infty} \sum_{m=-l}^l \left(A_{lm}^{el}(Q, Q) \frac{\eta_l(\varrho)}{\varrho} + a_{lm}^{el}(Q, Q) \frac{\psi_l(\varrho)}{\varrho} \right) Y_{lm}(\vartheta, \varphi). \quad (2.8b)$$

Die Funktion $\eta_l(\varrho)$ ist nur in (2.8b) enthalten, da sie ja nur bei der Entwicklung um den Quellpunkt Q auftreten kann. Die Koeffizienten in den entsprechenden Entwicklungen für Π^{mg} bezeichnen wir durch einen oberen Index mg .

Falls es sich um eine in den Quellpunkt Q einlaufende Wellenbewegung handelt, ist in (2.8b) die Funktion $\eta_l(\varrho)$ (2.5) durch $\zeta_l(\varrho)$ (2.6) zu ersetzen.

Es sei hier noch hervorgehoben, daß die Achsen der Koordinatensysteme in den beiden Punkten Q und P keineswegs parallel zueinander angenommen werden müssen.

Zusammenfassend können wir behaupten: In einem Raumgebiet, in dem ε und μ konstant sind, läßt sich ein beliebiges zeitlich harmonisch-periodisches und den Maxwell'schen Gleichungen (1.1) genügendes elektromagnetisches Feld in der Gestalt

$$\mathbf{E} = \mathbf{E}^{el} + \mathbf{E}^{mg}, \quad \mathbf{H} = \mathbf{H}^{el} + \mathbf{H}^{mg} \quad (2.9)$$

darstellen, wo \mathbf{E}^{el} , \mathbf{H}^{el} sich nach (2.1a) aus einem Potential Π^{el} und \mathbf{E}^{mg} , \mathbf{H}^{mg} sich nach (2.1b) aus einem Potential Π^{mg} berechnen läßt. Die Potentiale Π^{el} und analog auch Π^{mg} können durch Reihen von der Gestalt (2.8a) und (2.8b) mit $\eta_l(\varrho)$ oder $\zeta_l(\varrho)$ dargestellt werden.

§ 3. Herleitung des verallgemeinerten elektromagnetischen Reziprozitätstheorems

Wir bezeichnen mit R ein Raumgebiet, das sich eventuell auch ins Unendliche erstreckt und sonst von vollkommenen Leitern begrenzt wird. Die Materialkonstanten ε und μ sollen sich in R gegebenenfalls nur in Sprungflächen ändern, sonst aber im allgemeinen konstant sein. In R seien zwei elektromagnetische Felder \mathbf{E}_1 , \mathbf{H}_1 und \mathbf{E}_2 , \mathbf{H}_2 gegeben, die je eine Strahlungsquelle in dem Raumpunkte Q_1 bzw. Q_2 besitzen. Dabei soll \mathbf{E}_1 , \mathbf{H}_1 eine aus dem Quellpunkt Q_1 auslaufende und \mathbf{E}_2 , \mathbf{H}_2 eine in den Quellpunkt Q_2 einlaufende Wellenbewegung darstellen. Ferner setzen wir von diesen beiden elektromagnetischen Feldern voraus, daß in den Sprungflächen von ε und μ die Tangentialkomponenten von \mathbf{E} und \mathbf{H} stetig sind und daß an den aus vollkommenen Leitern bestehenden Begrenzungsflächen die Tangentialkomponenten von \mathbf{E} verschwinden. Im Unendlichen sollen beide elektromagnetischen Felder die Sommerfeldsche Endlichkeits- und ferner \mathbf{E}_1 , \mathbf{H}_1 die Ausstrahlungsbedingung (1.5) und \mathbf{E}_2 , \mathbf{H}_2 die Einstrahlungsbedingung (1.6) erfüllen,

Im Lorentzschen Integralsatz (1.3) verschwinden dann die Integrale über die Sprung- und Begrenzungsflächen und auch über die „unendlich ferne Fläche“. Die Integration ist daher in (1.3) lediglich über zwei die Quellpunkte Q_1 und Q_2 umschließende Flächen K_1 bzw. K_2 zu erstrecken, die wir als kleine Kugeln mit den Mittelpunkten in Q_1 bzw. Q_2 voraussetzen wollen. Es gilt also

$$\int_{K_1+K_2} [(\mathbf{E}_1 \times \mathbf{H}_2)_n + (\mathbf{E}_2^* \times \mathbf{H}_1)_n] df = 0. \quad (3.1)$$

Da nach (2.9)

$$\mathbf{E}_1 \times \mathbf{H}_2^* = \mathbf{E}_1^{el} \times \mathbf{H}_2^{el*} + \mathbf{E}_1^{mg} \times \mathbf{H}_2^{mg*} + \mathbf{E}_1^{el} \times \mathbf{H}_2^{mg*} + \mathbf{E}_1^{mg} \times \mathbf{H}_2^{el*} \quad (3.2)$$

ist und ein analoger Ausdruck für $\mathbf{E}_2^* \times \mathbf{H}_1$ gilt, so zerfällt in (3.1) jedes der beiden Integrale über K_1 bzw. K_2 in vier Integrale, die wir für die Kugelfläche K_1 im folgenden mit (I), (II), (III), (IV) bezeichnen. Weiter kann dann jedes dieser vier Integrale, wenn die elektromagnetischen Felder nach § 2 in Reihen entwickelt werden, durch eine Doppelreihe von Integralen dargestellt werden. Wir erhalten also für das Integral über K_1 insgesamt vier Gruppen von Doppelreihen. Zuerst behandeln wir das Integral

$$(I) = \int_{K_1} [(\mathbf{E}_1^{el} \times \mathbf{H}_2^{el*})_n + (\mathbf{E}_2^{el*} \times \mathbf{H}_1^{el})_n] df. \quad (3.3)$$

Verwenden wir räumliche Polarkoordinaten r, ϑ, φ , deren Ursprung im Mittelpunkte von K_1 liegt, so wird (da ja $\mathbf{n} = -\mathbf{r}/r$ die äußere Normale von K_1 als Begrenzung des Raumes R bedeutet):

$$(\mathbf{E}_1^{el} \times \mathbf{H}_2^{el*})_n = \mathbf{E}_{1\varphi}^{el} \mathbf{H}_{2\vartheta}^{el*} - \mathbf{E}_{1\vartheta}^{el} \mathbf{H}_{2\varphi}^{el*}. \quad (3.4)$$

Um zunächst ein einzelnes Glied, der (I) entsprechenden Doppelreihe zu berechnen, müssen wir voraussetzen, daß $\mathbf{E}_1^{el}, \mathbf{H}_1^{el}$ und $\mathbf{E}_2^{el}, \mathbf{H}_2^{el}$ sich mit Hilfe der Potentiale

$$\Pi_1^{el} = f_1(\varrho) Y_{lm}(\vartheta, \varphi) \text{ bzw. } \Pi_2^{el} = f_2(\varrho) Y_{l'm'}(\vartheta, \varphi) \quad (3.5)$$

darstellen lassen, in denen

$$f_1(\varrho) = A_{lm}^{el}(Q_1, Q_1) \frac{\eta_l(\varrho)}{\varrho} + a_{lm}^{el}(Q_1, Q_1) \frac{\psi_l(\varrho)}{\varrho}, \quad (3.6a)$$

$$f_2(\varrho) = a_{l'm'}^{el}(Q_2, Q_1) \frac{\psi_{l'}(\varrho)}{\varrho} \quad (3.6b)$$

bedeutet. Das Potential Π_1^{el} wird nämlich in der Umgebung seines Quellpunktes Q_1 also nach (2.8b) entwickelt, während Π_2^{el} in der Umgebung des von seinem Quellpunkte Q_2 verschiedenen Raumpunktes Q_1 also nach (2.8a) dargestellt werden muß.

Unter diesen Voraussetzungen wird gemäß (2.1), (3.4), (3.5) und (3.6)

$$(\mathbf{E}_1^{el} \times \mathbf{H}_2^{el*})_n + (\mathbf{E}_2^{el*} \times \mathbf{H}_1^{el})_n = N(Y_{lm}, Y_{l'm'}^*) M(f_1(\varrho), f_2^*(\varrho)), \quad (3.7)$$

wo

$$N(Y_{lm}, Y_{l'm'}^*) = \frac{1}{\sin^2 \vartheta} \frac{\partial Y_{lm}}{\partial \varphi} \frac{\partial Y_{l'm'}^*}{\partial \varphi} + \frac{\partial Y_{lm}}{\partial \vartheta} \frac{\partial Y_{l'm'}^*}{\partial \vartheta}, \quad (3.8a)$$

$$M(f_1(\varrho), f_2^*(\varrho)) = -\frac{i \kappa_e k}{\varrho} \left\{ f_1 \frac{d(\varrho f_2^*)}{d\varrho} - f_2^* \frac{d(\varrho f_1)}{d\varrho} \right\}. \quad (3.8b)$$

Setzen wir nun in (I) $df = r^2 d\omega$, wo $d\omega$ das Flächenelement der Einheitskugel ε und r den Radius der Kugel K_1 bedeutet, so folgt aus (3.3) und (3.7)

$$(I) = \sum_{l,m} \sum_{l',m'} r^2 M(f_1, f_2^*) \int_{\varepsilon} N(Y_{lm}, Y_{l'm'}^*) d\omega. \quad (3.9)$$

Um hier zunächst die Integrale über die Einheitskugel ε anzugeben, schreiben wir die identische Relation

$$\operatorname{div}(Y_{l'm'}^* \operatorname{grad} Y_{lm}) = \operatorname{grad} Y_{lm} \operatorname{grad} Y_{l'm'}^* + Y_{l'm'}^* \Delta Y_{lm}$$

in sphärischen Polarkoordinaten hin. Da

$$\Delta Y_{lm} = -\frac{l(l+1)}{r^2} Y_{lm},$$

so erhalten wir mit Rücksicht auf (3.8a) die Beziehung

$$\begin{aligned} \frac{1}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \left(\sin \vartheta Y_{l'm'}^* \frac{\partial Y_{lm}}{\partial \vartheta} \right) + \frac{1}{\sin \vartheta} \frac{\partial}{\partial \varphi} \left(Y_{l'm'}^* \frac{\partial Y_{lm}}{\partial \varphi} \right) \\ = N(Y_{lm}, Y_{l'm'}^*) - l(l+1) Y_{lm} Y_{l'm'}^*. \end{aligned}$$

Bei der Integration über die Einheitskugel ε verschwindet die linke Seite dieser Relation ($d\omega = \sin \vartheta d\vartheta d\varphi$) und es wird daher

$$\begin{aligned} \int_{\varepsilon} N(Y_{lm}, Y_{l'm'}^*) d\omega = l(l+1) \int_{\varepsilon} Y_{lm} Y_{l'm'}^* d\omega = l(l+1) \delta_{ll'} \delta_{mm'} K_{lm} \\ \text{wo } K_{lm} = 2\pi \int_0^\pi (P_l^m(\cos \vartheta))^2 \sin \vartheta d\vartheta \end{aligned} \quad (3.10)$$

das Quadrat des Normierungsnenners der Kugelflächenfunktion Y_{lm} bezeichnet.

Um (I) anzugeben, muß noch $M(f_1, f_2^*)$ berechnet werden. Aus (3.6a), (3.6b) und (3.8b) folgt

$$M(f_1, f_2^*) = A_{lm}^{el} (Q_1, Q_1) a_{lm}^{el*} (Q_2, Q_1) M\left(\frac{\eta_l}{\varrho}, \frac{\psi_l}{\varrho}\right), \quad (3.11)$$

wenn wir mit Rücksicht auf (3.10) $l' = l$ und $m' = m$ setzen. Aus der Differentialrelation für die Zylinderfunktionen

$$\frac{d Z_n(\varrho)}{d\varrho} = -\frac{n}{\varrho} Z_n(\varrho) + Z_{n-1}(\varrho)$$

sowie der Funktionalgleichung

$$J_{n-1}(\varrho) H_n^{(1)}(\varrho) - J_n(\varrho) H_{n-1}^{(1)}(\varrho) = \frac{2}{i\pi\varrho}$$

folgt nun die Beziehung

$$\eta_l \frac{d}{d\varrho} \psi_l - \psi_l \frac{d}{d\varrho} \eta_l = -i.$$

Es wird somit

$$M\left(\frac{\eta_l}{\varrho}, \frac{\psi_l}{\varrho}\right) = -\frac{\kappa_s k}{\varrho^2}. \quad (3.12)$$

Wir erhalten daher aus (1.2), (3.9), (3.10), (3.11) und (3.12) für (I) (3.3) den Ausdruck

$$(I) = - \sum_{l=0}^{\infty} \sum_{m=-l}^l l(l+1) \sqrt{\frac{\varepsilon}{\mu}} A_{lm}^{el}(Q_1, Q_1) a_{lm}^{el*}(Q_2, Q_1) K_{lm}. \quad (3.13)$$

Auf dem gleichen Wege ergibt sich für das Integral (vgl. (3.3))

$$(II) = \int_{K_1} [(E_1^{mg} \times H_2^{mg*})_n + (E_2^{mg*} \times H_1^{mg})_n] df$$

die Reihenentwicklung

$$(II) = - \sum_{l=0}^{\infty} \sum_{m=-l}^l l(l+1) \sqrt{\frac{\mu}{\varepsilon}} A_{lm}^{mg}(Q_1, Q_1) a_{lm}^{mg*}(Q_2, Q_1) K_{lm}. \quad (3.14)$$

Hingegen kann man zeigen, daß die beiden Integrale

$$(III) = \int_{K_1} [(E_1^{el} \times H_2^{mg*})_n + (E_2^{mg*} \times H_1^{el})_n] df \quad \text{und}$$

$$(IV) = \int_{K_1} [(E_1^{mg} \times H_2^{el*})_n + (E_2^{el*} \times H_1^{mg})_n] df$$

verschwinden. Wir führen den Nachweis für das Integral (III) durch. Es genügt ein einzelnes Glied der Doppelreihe zu betrachten, die (III) darstellt. Zu diesem Zwecke setzen wir voraus, daß E_1^{el} , H_1^{el} und E_2^{mg} , H_2^{mg} durch die beiden Potentiale

$$H_1^{el} = f_3(\varrho) Y_{lm}(\vartheta, \varphi) \quad \text{bzw.} \quad H_2^{mg} = f_4(\varrho) Y_{l'm'}(\vartheta, \varphi)$$

gegeben werden. Man erhält dann

$$(\mathbf{E}_1^{el} \times \mathbf{H}_2^{mg*})_n + (\mathbf{E}_2^{mg*} \times \mathbf{H}_1^{el})_n = O(Y_{lm}, Y_{l'm'}^*) P(f_3, f_4^*)$$

wo

$$O(Y_{lm}, Y_{l'm'}^*) = \frac{1}{\sin \vartheta} \left(\frac{\partial Y_{lm}}{\partial \varphi} \frac{\partial Y_{l'm'}^*}{\partial \vartheta} - \frac{\partial Y_{lm}}{\partial \vartheta} \frac{\partial Y_{l'm'}^*}{\partial \varphi} \right),$$

$$P(f_3, f_4^*) = k^2 \left(f_3 f_4^* + \frac{1}{\varrho^2} \frac{d(\varrho f_3)}{d\varrho} \frac{d(\varrho f_4^*)}{d\varrho} \right).$$

Um zu zeigen, daß (III) verschwindet, genügt es den Nachweis zu erbringen, daß

$$\int_s O(Y_{lm}, Y_{l'm'}^*) d\omega = 0$$

ist für beliebige l, m und l', m' . Dies folgt aus der Tatsache, daß wegen $\text{rot grad} = 0$ die identische Beziehung

$$\text{rot}(Y_{lm} \text{grad } Y_{l'm'}^*) = \text{grad } Y_{lm} \times \text{grad } Y_{l'm'}^*$$

gilt, deren r -Komponente in sphärischen Polarkoordinaten ausgedrückt

$$\text{rot}_r(Y_{lm} \text{grad } Y_{l'm'}^*) = -\frac{1}{r^2} O(Y_{lm}, Y_{l'm'}^*)$$

lautet. Damit ist unser Ziel erreicht. Es ist ja dann

$$\int_s O(Y_{lm}, Y_{l'm'}^*) d\omega = \int_{K_1} \text{rot}_n(Y_{lm} \text{grad } Y_{l'm'}^*) df$$

und das hier auftretende Integral über K_1 verschwindet wegen $\text{div rot} = 0$.

Ebenso kann man zeigen, daß auch (IV) = 0 ist.

Im ganzen erhalten wir somit mit Rücksicht auf (3.13) und (3.14) für den Beitrag der Kugel K_1 zum Integral (3.1) den Ausdruck

$$-\sum_{l=0}^{\infty} \sum_{m=-l}^l l(l+1) K_{lm} \left\{ \sqrt{\frac{\varepsilon}{\mu}} A_{lm}^{el}(Q_1, Q_1) a_{lm}^{el*}(Q_2, Q_1) + \right. \\ \left. + \sqrt{\frac{\mu}{\varepsilon}} A_{lm}^{mg}(Q_1, Q_1) a_{lm}^{mg*}(Q_2, Q_1) \right\}. \quad (3.15)$$

Der Beitrag der Kugel K_2 zum Integral (3.1) berechnet sich ganz ebenso wie der Beitrag der Kugel K_1 . Dabei ist nur zu berücksichtigen daß das elektromagnetische Feld $\mathbf{E}_2, \mathbf{H}_2$ durch eine im Quellpunkt Q_2 einlaufende Welle gegeben wird und daher in seinem Potential die Funktion $\zeta_l(\varrho)$ (2.6) an Stelle von $\eta_l(\varrho)$ (2.5) in $\mathbf{E}_1, \mathbf{H}_1$ tritt. Die Rechnung ergibt für den Beitrag der Kugel K_2 zum Integral (3.1) den konjugiert-komplexen Wert des Ausdruckes (3.15) in dem die Indizes 1 und 2 vertauscht und das Vorzeichen geändert wurde. Man erhält daher aus (3.1) das ge-

suchte elektromagnetische Reziprozitätstheorem in der Gestalt

$$\begin{aligned}
 & \sum_{l=0}^{\infty} \sum_{m=-l}^l l(l+1) K_{lm} \left\{ \sqrt{\frac{\varepsilon_1}{\mu_1}} A_{lm}^{el}(Q_1, Q_1) a_{lm}^{el*}(Q_2, Q_1) + \right. \\
 & \quad \left. + \sqrt{\frac{\mu_1}{\varepsilon_1}} A_{lm}^{mg}(Q_1, Q_1) a_{lm}^{mg*}(Q_2, Q_1) \right\} = \\
 & = \sum_{l=0}^{\infty} \sum_{m=-l}^l l(l+1) K_{lm} \left\{ \sqrt{\frac{\varepsilon_2}{\mu_2}} A_{lm}^{el*}(Q_2, Q_2) a_{lm}^{el}(Q_1, Q_2) + \right. \\
 & \quad \left. + \sqrt{\frac{\mu_2}{\varepsilon_2}} A_{lm}^{mg*}(Q_2, Q_2) a_{lm}^{mg}(Q_1, Q_2) \right\}.
 \end{aligned} \tag{3.16}$$

Der Tatsache, daß ε und μ in den beiden Raumpunkten Q_1 und Q_2 verschieden sein können, wurde in (3.16) dadurch Rechnung getragen, daß diese beiden Materialkonstanten mit den entsprechenden Indizes versehen wurden.

§ 4. Diskussion der Rekursionsformel

Für die folgenden Überlegungen setzen wir voraus, daß das elektromagnetische Feld $\mathbf{E}_2, \mathbf{H}_2$, das eine in ihrem Quellpunkte Q_2 einlaufende elektromagnetische Wellenbewegung darstellt, nur eine einzige, einem speziellen Indexpaar l_0, m_0 entsprechende elektrische oder magnetische Multipolquelle mit der Amplitude $A_{l_0 m_0}^{el}(Q_0, Q_0)$ bzw. $A_{l_0 m_0}^{mg}(Q_2, Q_2)$ besitzt. Im ersten Falle verschwinden dann alle übrigen anderen Indizes l, m tragende $A_{lm}^{el}(Q_2, Q_2)$ sowie ausnahmslos alle $A_{lm}^{mg}(Q_2, Q_2)$. Im zweiten Falle sind alle mit anderen Indizes versehenen $A_{lm}^{mg}(Q_2, Q_2) = 0$, sowie ausnahmslos alle $A_{lm}^{el}(Q_2, Q_2) = 0$. Das allgemeine Reziprozitätstheorem (3.16) ergibt daher in diesen beiden Spezialfällen die nachstehenden Reziprozitätstheoreme

$$\begin{aligned}
 & l_0(l_0+1) K_{l_0 m_0} \sqrt{\frac{\varepsilon_2}{\mu_2}} A_{l_0 m_0}^{el*}(Q_2, Q_2) a_{l_0 m_0}^{el}(Q_1, Q_2) = \\
 & = \sum_{l=0}^{\infty} \sum_{m=-l}^l l(l+1) K_{lm} \left\{ \sqrt{\frac{\varepsilon_1}{\mu_1}} A_{lm}^{el}(Q_1, Q_1) a_{lm}^{el*}(Q_2, Q_1) + \right. \\
 & \quad \left. + \sqrt{\frac{\mu_1}{\varepsilon_1}} A_{lm}^{mg}(Q_1, Q_1) a_{lm}^{mg*}(Q_2, Q_1) \right\},
 \end{aligned} \tag{4.1}$$

$$\begin{aligned}
 & l_0(l_0+1) K_{l_0 m_0} \sqrt{\frac{\mu_2}{\varepsilon_2}} A_{l_0 m_0}^{mg*}(Q_2, Q_2) a_{l_0 m_0}^{mg}(Q_1, Q_2) = \\
 & = \sum_{l=0}^{\infty} \sum_{m=-l}^l l(l+1) K_{lm} \left\{ \sqrt{\frac{\varepsilon_1}{\mu_1}} A_{lm}^{el}(Q_1, Q_1) a_{lm}^{el*}(Q_2, Q_1) + \right. \\
 & \quad \left. + \sqrt{\frac{\mu_1}{\varepsilon_1}} A_{lm}^{mg}(Q_1, Q_1) a_{lm}^{mg*}(Q_2, Q_1) \right\}.
 \end{aligned} \tag{4.2}$$

Es muß darauf hingewiesen werden, daß die Koeffizienten $a_{lm}^{el}(Q_2, Q_1)$ und $a_{lm}^{mg}(Q_2, Q_1)$ in jeder der beiden Relationen (4.1) und (4.2) zu elektromagnetischen Feldern mit verschiedenen Strahlungsquellen gehören und daher auch verschiedene Werte haben. Hingegen kann sowohl (4.1) als auch (4.2) selbstverständlich auf das gleiche elektromagnetische Feld $\mathbf{E}_1, \mathbf{H}_1$ angewendet werden.

Um zu zeigen, in welcher Weise das Reziprozitätstheorem (4.1) bzw. (4.2) zur Berechnung von Multipolfeldern verwendet werden kann, setzen wir ferner voraus, daß das elektromagnetische Feld $\mathbf{E}_2, \mathbf{H}_2$, das in (4.1) bzw. in (4.2) auftritt, bekannt ist. Wir können dann auch die Koeffizienten $a_{lm}^{el}(Q_2, Q_1)$ und $a_{lm}^{mg}(Q_2, Q_1)$, die die Entwicklung dieser Felder in dem Raumpunkte Q_1 darstellen, sowohl im Falle (4.1) als auch im Falle (4.2) als bekannt ansehen. Denken wir uns nun ein elektromagnetisches Feld $\mathbf{E}_1, \mathbf{H}_1$ durch die Amplituden $A_{lm}^{el}(Q_1, Q_1)$, $A_{lm}^{mg}(Q_1, Q_1)$ seiner Multipolquellen im Quellpunkte Q_1 definiert. Wir können dann mit Hilfe von (4.1) bzw. (4.2) die Koeffizienten $a_{l_0 m_0}^{el}(Q_1, Q_2)$ bzw. $a_{l_0 m_0}^{mg}(Q_1, Q_2)$ seiner Entwicklung nach elektrischen bzw. magnetischen Multipolfeldern im Raumpunkte Q_2 angeben.

Will man nun den Verlauf des Feldes $\mathbf{E}_1, \mathbf{H}_1$ in der Umgebung des Punktes Q_2 bestimmen, so muß man alle Koeffizienten $a_{lm}^{el}(Q_1, Q_2)$ und $a_{lm}^{mg}(Q_1, Q_2)$ der Entwicklung von $\mathbf{E}_1, \mathbf{H}_1$ im Punkte Q_2 kennen. Es ist dann erforderlich die beiden Reziprozitätstheoreme (4.1) und (4.2) für alle l_0, m_0 anzuwenden. Man muß dann also die Felder $\mathbf{E}_2, \mathbf{H}_2$ mit elektrischen bzw. magnetischen Multipolen beliebig hoher Ordnung zur Verfügung haben.

Viel einfacher ist das Problem die elektrischen und magnetischen Feldstärken des Feldes $\mathbf{E}_1, \mathbf{H}_1$, das beliebig vorgegebene Multipolquellen im Punkte Q_1 besitzt, nur in dem Punkte Q_2 zu berechnen. Diese Feldstärken werden, wie in § 5 klar werden wird (vgl. (5.8)), durch die Koeffizienten $a_{lm}^{el}(Q_1, Q_2)$ und $a_{lm}^{mg}(Q_1, Q_2)$ ($m = 0, \pm 1$) bestimmt. Wie aus (4.1) und (4.2) hervorgeht, ist es zu diesem Zwecke nur erforderlich Felder $\mathbf{E}_2, \mathbf{H}_2$ mit nichtverschwindenden $A_{lm}^{el}(Q_2, Q_2)$ und $A_{lm}^{mg}(Q_2, Q_2)$ ($m = 0, \pm 1$) zur Verfügung zu haben d. h. elektromagnetische Felder, die einer elektrischen und einer magnetischen Dipolstrahlung entsprechen, ohne Rücksicht auf die Ordnung der elektrischen und magnetischen Multipolquellen des Feldes $\mathbf{E}_1, \mathbf{H}_1$, das berechnet werden soll.

§ 5. Berechnung einiger Koeffizienten a_{lm}^{el} und a_{lm}^{mg} aus den elektromagnetischen Feldstärken

Bei den Kosselschen Interferenzversuchen beobachtet man praktisch im Unendlichen die Beugungsfransen, die durch die Beugung der von einem Atom eines Kristallgitters emittierten Röntgenstrahlung an anderen Atomen des gleichen Kristallgitters entstehen. Im Falle, wo die Röntgenstrahlung von einem elektrischen Dipol herrührt, hat Max von Laue (1935, 1937, 1941, 1948) eine sehr elegante Lösung dieses Problems gegeben. Er hat nämlich auf die bekannte Lösung des Problems der Reflexion einer ebenen Röntgenwelle an einem Kristallgitter das Reziprozitätstheorem

für die elektrische Dipolstrahlung angewendet. Da man annehmen kann, daß die einfallende ebene Welle durch eine im Unendlichen liegende Dipolquelle verursacht wird, kann man das elektromagnetische Feld des Reflexionsproblems als das Feld ansehen, das in unserer Formulierung des verallgemeinerten Reziprozitätstheorems mit \mathbf{E}_2 , \mathbf{H}_2 bezeichnet wird. Durch Anwendung des Reziprozitätstheorems für die elektrische Dipolstrahlung kann man sodann das elektromagnetische Feld \mathbf{E}_1 , \mathbf{H}_1 einer in einem Gitterpunkte liegenden Dipolquelle am Orte des Quellpunktes von \mathbf{E}_2 , \mathbf{H}_2 d. h. im Unendlichen angeben.

In der gleichen Weise kann man unter Zuhilfenahme der gleichen Lösung des Reflexionsproblems durch Anwendung des für beliebige Multipolquellen verallgemeinerten Reziprozitätstheorems den Fall erledigen, wo ein dem Kristallgitter angehörendes Atom irgend eine Multipolstrahlung aussendet. In einem jeden solchen Falle steht man vor der Aufgabe die im betrachteten Multipolfalle im Reziprozitätstheorem (4.1) oder (4.2) auftretenden Koeffizienten $a_{lm}^{el}(Q_2, Q_1)$ und $a_{lm}^{mg}(Q_2, Q_1)$ aus den Feldstärken \mathbf{E}_2 , \mathbf{H}_2 zu bestimmen.

Im Falle der elektrischen und magnetischen Dipol- und der elektrischen Quadrupolstrahlung, die bei vielen physikalischen und technischen Problemen auftreten, ist die Kenntnis der Koeffizienten

$$a_{lm}^{el}(Q_2, Q_1) \quad (l = 1, 2), \quad (5.1a) \quad a_{lm}^{mg}(Q_2, Q_1) \quad (5.1b)$$

erforderlich.

Die Koeffizienten $a_{00}^{el}(Q_2, Q_1)$, $a_{00}^{mg}(Q_2, Q_1)$ können wir gleich Null setzen, da sie ebenso wie die Koeffizienten $A_{00}^{el}(Q_i, Q_i)$, $A_{00}^{mg}(Q_i, Q_i)$ ($i = 1, 2$) in der Entwicklung von \mathbf{E}_i , \mathbf{H}_i ($i = 1, 2$) überhaupt nicht auftreten. In den Entwicklungen der zugehörigen Potentiale enthalten die entsprechenden Glieder mit Rücksicht auf $Y_{00}(\vartheta, \varphi) = \text{const}$ nur die Funktionen $\psi_0(\varrho)$, $\eta_0(\varrho)$ oder $\zeta_0(\varrho)$. Gemäß (2.1) verschwinden daher die Radialkomponenten E_r^{el} und H_r^{mg} , weil ja $E_r^{el} = 0$ oder $H_r^{mg} = 0$ geradezu die Differentialgleichung darstellt, der diese Funktionen genügen. Die übrigen Komponenten von \mathbf{E}^{el} , \mathbf{H}^{el} und \mathbf{E}^{mg} , \mathbf{H}^{mg} sind aber gemäß (2.1) gleich Null, weil die Glieder mit den Koeffizienten a_{00}^{el} und a_{00}^{mg} mit Rücksicht auf $Y_{00}(\vartheta, \varphi) = \text{const}$ von ϑ und φ nicht abhängen. Diese Glieder besitzen daher eine Bedeutung nur für die Entwicklung der Potentiale Π^{el} und Π^{mg} , nicht aber für die Entwicklung des elektromagnetischen Feldes.

Der Zahlenwert der Koeffizienten (5.1) hängt selbstverständlich von der Normierung der in $Y_{lm}(\vartheta, \varphi)$ (2.4) enthaltenen zugeordneten Kugelfunktionen $P_l^m(\xi)$ ab. Wir entscheiden uns für die von C. G. Darwin angegebene Normierung, setzen also

$$P_0^0 = 1; P_1^0 = \xi, P_1^1 = (1 - \xi^2)^{1/2}; P_2^0 = 3\xi^2 - 1, P_2^1 = (1 - \xi^2)^{1/2} 3\xi, P_2^2 = 3(1 - \xi^2) \quad (5.2)$$

und nehmen dementsprechend an, daß $P_l^{-m}(\xi) = (-1)^m P_l^m(\xi)$ ist.

Um zunächst die „elektrischen“ Koeffizienten (5.1a) anzugeben, ist es notwendig die Feldstärken \mathbf{E}_2^{el} , \mathbf{H}_2^{el} nach den Koordinaten x, y, z bis einschließlich der linearen Glieder zu entwickeln. Aus (2.2a) ist ersichtlich, daß hierzu nur die Kenntnis der

linearen und der quadratischen Glieder von Π^{el} erforderlich ist. Man muß daher in der Entwicklung (2.8a) des Potentials Π^{el} in der Umgebung eines regulären Punktes in den Funktionen $\psi_l(\varrho)$ nur noch dritte Potenzen von ϱ berücksichtigen. Gemäß (2.7) genügt es daher $\psi_1(\varrho) = \varrho^2/3$, $\psi_2(\varrho) = \varrho^3/15$ und alle übrigen $\psi_l(\varrho) = 0$ zu setzen. Führen wir die Bezeichnung

$$\Pi_{lm}^{el} = a_{lm}^{el}(Q_2, Q_1) \frac{\psi_l(\varrho)}{\varrho} Y_{lm}(\vartheta, \varphi) \quad (5.3)$$

ein, so haben mit Rücksicht auf (5.2) die von uns benötigten Π_{lm}^{el} , wenn wir sie bis einschließlich der quadratischen Glieder in x, y, z angeben, die Gestalt

$$\begin{aligned} \Pi_{1,-1}^{el} &= -a_{1,-1}^{el} \frac{1}{3} k (x - iy), & \Pi_{10}^{el} &= a_{10}^{el} \frac{1}{3} k z, & \Pi_{11}^{el} &= a_{11}^{el} \frac{1}{3} k (x + iy), \\ \Pi_{2,-2}^{el} &= a_{2,-2}^{el} \frac{1}{5} k^2 (x - iy)^2, & \Pi_{2,-1}^{el} &= -a_{2,-1}^{el} \frac{1}{5} k^2 (x - iy) z, \\ \Pi_{20}^{el} &= a_{20}^{el} \frac{1}{15} k^2 (2z^2 - x^2 - y^2), & \Pi_{21}^{el} &= a_{21}^{el} \frac{1}{5} k^2 (x + iy) z, \\ \Pi_{22}^{el} &= a_{22}^{el} \frac{1}{5} k^2 (x + iy)^2. \end{aligned} \quad (5.4)$$

Andere Π_{lm}^{el} kommen nicht in Frage, da ja das Π_{00}^{el} entsprechende elektromagnetische Feld verschwindet und die Π_{lm}^{el} (5.3) mit $l \geq 3$ vom mindestens dritten Grade in x, y, z sind.

Um die Formeln in (5.4) nicht allzu lang werden zu lassen, haben wir bei den hier auftretenden Koeffizienten $a_{lm}^{el}(Q_2, Q_1)$ die Klammerbezeichnungen (Q_2, Q_1) fortgelassen. Dies soll aus dem gleichen Grunde auch bei allen weiter unten anzugebenden Formeln geschehen. Man vergesse also nicht, daß sie sich auf ein elektromagnetisches Feld mit dem Quellpunkt in Q_2 beziehen, das wir in dem Raumpunkte Q_1 oder in seiner Umgebung betrachten.

Bezeichnet man die Π_{lm}^{el} (5.3) gemäß (2.2a) entsprechenden Feldstärken mit E_{lm}^{el} , H_{lm}^{el} , so erhält man aus den Potentialen (5.4) für sie die Ausdrücke

$$\begin{aligned} E_{1,-1}^{el} &= -a_{1,-1}^{el} \frac{2}{3} k (\mathbf{i} - \mathbf{j}), & H_{1,-1}^{el} &= -a_{1,-1}^{el} \frac{1}{3} k \kappa_e [-(\mathbf{i} - \mathbf{j}) z + \mathbf{k} (x - iy)], \\ E_{10}^{el} &= a_{10}^{el} \frac{2}{3} k \mathbf{k}, & H_{10}^{el} &= a_{10}^{el} \frac{1}{3} k \kappa_e [\mathbf{i} iy - \mathbf{j} ix], \\ E_{11}^{el} &= a_{11}^{el} \frac{2}{3} k (\mathbf{i} + \mathbf{j}), & H_{11}^{el} &= a_{11}^{el} \frac{1}{3} k \kappa_e [(\mathbf{i} + \mathbf{j}) z - \mathbf{k} (x + iy)], \\ E_{2,-2}^{el} &= a_{2,-2}^{el} \frac{6}{5} k^2 (\mathbf{i} - \mathbf{j}) (x - iy), & H_{2,-2}^{el} &= 0, \\ E_{2,-1}^{el} &= -a_{2,-1}^{el} \frac{3}{5} k^2 [(\mathbf{i} - \mathbf{j}) z + \mathbf{k} (x - iy)], & H_{2,-1}^{el} &= 0, \\ E_{20}^{el} &= a_{20}^{el} \frac{2}{5} k^2 [-\mathbf{i} x - \mathbf{j} y + \mathbf{k} 2z], & H_{20}^{el} &= 0, \\ E_{21}^{el} &= a_{21}^{el} \frac{3}{5} k^2 [(\mathbf{i} + \mathbf{j}) z + \mathbf{k} (x + iy)], & H_{21}^{el} &= 0, \\ E_{22}^{el} &= a_{22}^{el} \frac{6}{5} k^2 (\mathbf{i} + \mathbf{j}) (x + iy), & H_{22}^{el} &= 0, \end{aligned} \quad (5.5)$$

falls wir uns auf die in x, y, z linearen Glieder beschränken.

Um auch die magnetischen Koeffizienten $a_{lm}^{mg}(Q_2, Q_1)$ (5.1b) zu erhalten, müßten wir das magnetische Potential Π^{mg} in Potentiale Π_{lm}^{mg} aufteilen, die den elektrischen Potentialen Π_{ml}^{el} (5.3) entsprechen und sodann die aus den Π_{lm}^{mg} gemäß (2.2b) abzuleitenden Feldstärken $\mathbf{E}_{lm}^{mg}, \mathbf{H}_{lm}^{mg}$ berechnen. Es ist jedoch gar nicht notwendig diese Rechnungen durchzuführen, da, wie der Vergleich von (2.2b) mit (2.2a) lehrt, wir diese Feldstärken erhalten, wenn wir an Stelle von \mathbf{E}_{lm}^{el} bzw. \mathbf{H}_{lm}^{el} die Feldstärken \mathbf{H}_{lm}^{mg} bzw. $-\mathbf{E}_{lm}^{mg}$ treten lassen. Dabei ist gleichzeitig κ_s durch κ_μ zu ersetzen und man hat statt a_{lm}^{el} die Koeffizienten $a_{lm}^{mg}(Q_2, Q_1)$ zu verwenden. Für den Teil II der vorliegenden Arbeit benötigen wir von den elektrischen Feldstärken \mathbf{E}_{lm}^{mg} nur solche mit den in x, y, z linearen Gliedern und von den magnetischen Feldstärken \mathbf{H}_{lm}^{mg} nur solche mit konstanten Gliedern. Die in dieser Näherung nicht verschwindenden Feldstärken $\mathbf{E}_{lm}^{mg}, \mathbf{H}_{lm}^{mg}$ ergeben sich aus (5.5) zu

$$\begin{aligned} \mathbf{E}_{1,-1}^{mg} &= -a_{1,-1}^{mg} \frac{1}{3} k \kappa_\mu [(\mathbf{i} - \mathbf{j})z - \mathbf{k}(x - iy)], & \mathbf{H}_{1,-1}^{mg} &= -a_{1,-1}^{mg} \frac{2}{3} k (\mathbf{i} - \mathbf{j}), \\ \mathbf{E}_{10}^{mg} &= -a_{10}^{mg} \frac{1}{3} k \kappa_\mu (\mathbf{i}iy - \mathbf{j}ix), & \mathbf{H}_{10}^{mg} &= a_{10}^{mg} \frac{2}{3} k \mathbf{k} \\ \mathbf{E}_{11}^{mg} &= -a_{11}^{mg} \frac{1}{3} k \kappa_\mu [(\mathbf{i} + \mathbf{j})z - \mathbf{k}(x + iy)], & \mathbf{H}_{11}^{mg} &= a_{11}^{mg} \frac{2}{3} k (\mathbf{i} + \mathbf{j}). \end{aligned} \quad (5.6)$$

Das gesamte vom Quellpunkte Q_2 herrührende elektromagnetische Feld erhalten wir in dem Raumpunkte Q_1 , wenn wir die Feldstärken (5.5) und (5.6) zueinander addieren:

$$\begin{aligned} E_x + iE_y &= -a_{1,-1}^{el} \frac{4}{3} k + a_{2,-2}^{el} \frac{12}{5} k^2 (x - iy) - a_{2,-1}^{el} \frac{6}{5} k^2 z - \\ &\quad - a_{20}^{el} \frac{2}{5} k^2 (x + iy) - a_{1,-1}^{mg} \frac{2}{3} k \kappa_\mu z - a_{10}^{mg} \frac{1}{3} k \kappa_\mu (x + iy), \\ E_x - iE_y &= a_{11}^{el} \frac{4}{3} k - a_{20}^{el} \frac{2}{5} k^2 (x - iy) + a_{21}^{el} \frac{6}{5} k^2 z + a_{22}^{el} \frac{12}{5} k^2 (x + iy) + \\ &\quad + a_{10}^{mg} \frac{1}{3} k \kappa_\mu (x - iy) - a_{11}^{mg} \frac{2}{3} k \kappa_\mu z, \\ E_z &= a_{10}^{el} \frac{2}{3} k - a_{2,-1}^{el} \frac{3}{5} k^2 (x - iy) + a_{20}^{el} \frac{4}{5} k^2 z + a_{21}^{el} \frac{3}{5} k^2 (x + iy) + \\ &\quad + a_{1,-1}^{mg} \frac{1}{3} k \kappa_\mu (x - iy) + a_{11}^{mg} \frac{1}{3} k \kappa_\mu (x + iy), \\ H_x + iH_y &= -a_{1,-1}^{mg} \frac{4}{3} k, & H_x - iH_y &= a_{11}^{mg} \frac{4}{3} k, & H_z &= a_{10}^{mg} \frac{2}{3} k. \end{aligned} \quad (5.7)$$

Wir haben dabei bei der elektrischen Feldstärke \mathbf{E} nur die in x, y, z linearen und bei der magnetischen Feldstärke \mathbf{H} nur die konstanten Glieder berücksichtigt.

Aus (5.7) erhält man entweder unmittelbar oder durch Nullsetzen von x, y, z oder auch durch Bildung der Ableitungen $\frac{\partial}{\partial x} \pm i \frac{\partial}{\partial y}, \frac{\partial}{\partial z}$ für die Koeffizienten (5.1) die Ausdrücke

$$\begin{aligned} -\frac{4}{3} a_{1,-1}^{el} k &= E_x + iE_y, & \frac{2}{3} a_{10}^{el} k &= E_z, & \frac{4}{3} a_{11}^{el} k &= E_x - iE_y, \\ -\frac{4}{3} a_{1,-1}^{mg} k &= H_x + iH_y, & \frac{2}{3} a_{10}^{mg} k &= H_z, & \frac{4}{3} a_{11}^{mg} k &= H_x - iH_y, \end{aligned}$$

$$\begin{aligned}
\frac{24}{5} a_{2,-2}^{el} k^2 &= \left(\frac{\partial}{\partial x} + i \frac{\partial}{\partial y} \right) (E_x + iE_y), & \frac{12}{5} a_{2,-1}^{el} k^2 &= \frac{\partial}{\partial z} (E_x + iE_y) + \\
&+ \left(\frac{\partial}{\partial x} + i \frac{\partial}{\partial y} \right) E_z, & \frac{4}{5} a_{20}^{el} k^2 &= \frac{\partial E_x}{\partial z}, & \frac{12}{5} a_{21}^{el} k^2 &= \frac{\partial}{\partial z} (E_x - iE_y) + \\
&+ \left(\frac{\partial}{\partial x} - i \frac{\partial}{\partial y} \right) E_z, & \frac{24}{5} a_{22}^{el} k^2 &= \left(\frac{\partial}{\partial x} - i \frac{\partial}{\partial y} \right) (E_x - iE_y). \quad (5.8)
\end{aligned}$$

Die Koeffizienten (5.1) stellen das durch die Quelle Q_2 in dem Raumpunkte Q_1 verursachte Feld dar. Die in (5.8) auftretenden elektromagnetischen Feldstärken und ihre Ableitungen entsprechen daher dem Felde $\mathbf{E}_2, \mathbf{H}_2$ in dem Raumpunkte Q_1 . Selbstverständlich kann man die Beziehungen (5.8) auch dazu verwenden um die Koeffizienten $a_{lm}^{el}(Q_1, Q_2)$ ($l = 1, 2$) und $a_{lm}^{mg}(Q_1, Q_2)$ des Feldes $\mathbf{E}_1, \mathbf{H}_1$ mit dem Quellpunkt in Q_1 in dem Raumpunkte Q_2 darzustellen.

Da zwischen den elektromagnetischen Feldstärken und ihren Ableitungen die durch die Maxwell'schen Gleichungen (1.1) geforderten Beziehungen bestehen, kann man die Koeffizienten (5.1) auch noch in anderer Weise durch die elektromagnetischen Feldstärken ausdrücken, als dies in (5.8) geschehen ist. Wir haben uns für die einfachste Darstellung entschieden, in der die „elektrischen“ Koeffizienten a_{lm}^{el} durch die elektrischen und die „magnetischen“ Koeffizienten a_{lm}^{mg} durch die magnetischen Feldstärken gegeben werden.

Bemerkenswert ist vielleicht eine Ähnlichkeit im Aufbau der Koeffizienten a_{lm}^{el} und a_{lm}^{mg} (5.8) und im Aufbau der konjugiert-komplexen Werte der räumlichen Kugelfunktionen, die die gleichen Indizes l, m tragen und die z. B. in den Potentialen Π_{lm}^{el} (5.4) auftreten. Die Koeffizienten a_{lm}^{el} bzw. a_{lm}^{mg} werden nämlich aus den entsprechenden konjugiert-komplexen räumlichen Kugelfunktionen erhalten, wenn man in ihnen die Koordinaten x, y, z teils durch die Feldstärken E_x, E_y, E_z bzw. H_x, H_y, H_z , teils durch die Differentialoperatoren $\partial/\partial x, \partial/\partial y, \partial/\partial z$ ersetzt. Dies gilt auch im Falle des Koeffizienten a_{20}^{el} , wenn man beachtet, daß man mit Rücksicht auf $\text{div } \mathbf{E} = 0$ ihn auch in der Gestalt

$$\frac{12}{5} a_{20}^{el} k^2 = 2 \frac{\partial E_z}{\partial z} - \frac{\partial E_x}{\partial x} - \frac{\partial E_y}{\partial y}$$

darstellen kann. Um jedoch festzustellen, ob dieser Analogie eine tiefere Bedeutung zugrunde liegt, müßte man die den höheren Multipolen entsprechenden Koeffizienten a_{lm}^{el} und a_{lm}^{mg} durch die elektromagnetischen Feldstärken und ihre Ableitungen ausdrücken.

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SUR LES SPECTRES RAMANIENS DES SOLUTIONS DE PYRIDINE ET DE 2,6 — LUTIDINE DANS LES ACIDES SATURÉS.

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On a étudié les spectres ramanien des solutions de différentes concentrations de la pyridine dans l'acide acétique et l'acide formique, ainsi que les solutions équimolaires de la pyridine dans l'acide butyrique et de la 2,6 — lutidine dans les mêmes acides saturés. On a constaté, que les variations du spectre de la pyridine et de la 2,6 — lutidine sous l'influence des acides formique et butyrique sont analogiques aux variations observées auparavant dans les spectres des solutions de la pyridine dans l'acide acétique. (Mierzecki 1953, 1955a). En particulier on observe des raies nouvelles correspondant aux pulsations du noyau (1007 K environ) et aux oscillations des liaisons C—H (3070 K environ) dans les molécules de la pyridine qui forment des complexes avec les molécules des acides.

Les mesures d'intensité de la raie 1003 K en fonction de la concentration des solutions indiquent, que le complexe qui se forme dans les solutions étudiées se compose d'une molécule de pyridine et d'une molécule d'acide.

On a montré aussi, que l'apparition de la raie de fréquence 1020 K qui a été observée dans les spectres de la pyridine dans l'acide acétique (Mierzecki 1955a, 1956) dépend de la présence d'une certaine quantité d'eau dans les solutions étudiées. Cette raie forme une modification d'une des raies de la pyridine.

I. Introduction

Les systèmes bases pyridiniques — acides saturés présentent le cas, où il existe des interactions intermoléculaires prédominantes. Dans des systèmes pareil même la formation de complexes est possible. En vue de ces effets plusieurs chercheurs ont étudié dans le système pyridine — acide acétique les changements de différentes propriétés physico-chimiques en fonction de la concentration. À partir des points particuliers des courbes qui représentent ces fonctions (extremums, points d'inflexion), ils ont essayé de déduire des conclusions concernant la composition des complexes. Selon la propriété étudiée, différents auteurs proposent différentes compo-

tions des complexes. La proposition la plus souvent rencontrée c'est 1 molécule de pyridine pour 4 molécules d'acide. D'après d'autres propositions les nombres de molécules de ces deux substances dans un complexe se comportent comme 3:2, 2:3, 1:3. Les études crioscopiques seules (Swearingen, Randal, Ross 1934) montrent, que le complexe qui se forme dans les solutions de la pyridine et de l'acide acétique, doit être composé d'un nombre égal de molécules de pyridine et d'acide acétique.

Les fortes interactions intermoléculaires qui existent dans les solutions doivent se manifester aussi par des changements dans les spectres ramanien. Les résultats des mesures de fréquence des raies dans les spectres des solutions de la pyridine et de l'acide acétique de différentes concentrations obtenus par l'auteur ont été publiés auparavant (Mierzecki 1953, 1955 a, b). Les résultats obtenus en même temps par Lakshmanan (1954), Chiorboli (1957) et Schwab et Glatzer (1957) sont en accord avec les résultats de l'auteur.

Il était intéressant d'étudier aussi les spectres des solutions de la pyridine et de la 2,6-diméthylpyridine (2,6-lutidine) dans d'autres acides saturés pour chercher des changements analogues des spectres. On a étudié alors les spectres des solutions équimolaires de la pyridine dans les acides formique et n-butyrique, ainsi que les spectres des solutions équimolaires de la 2,6-lutidine dans les acides formique, acétique et n-butyrique.

II. Expérimentale

a) Mesures de fréquence des raies

Les spectres ont été étudiés par la méthode photographique. Les détails de préparation des solutions de la pyridine et de l'acide acétique, ainsi que de mesure de la fréquence des raies ont été décrites auparavant (Mierzecki 1953, 1955a, 1957). Les solutions équimolaires des bases pyridiniques avec des acides ont été préparées en ajoutant à la pyridine distillée une quantité équivalente d'acide.

On a étudié aussi les spectres des solutions de la pyridine et de l'acide formique contenant 7, 9, 20 et 35% mole de pyridine. Les substances ont été soigneusement deshydratées et des précautions spéciales ont été prises pour éviter l'absorption de l'eau de l'atmosphère.

b) Mesures d'intensité des raies

On a étudié la variation d'intensité de quelques raies dans les spectres des solutions de la pyridine dans l'acide acétique en fonction de la concentration.

Les méthodes photographiques de mesure et de comparaison de l'intensité des raies Raman dans les spectres des solutions de différentes concentrations sont très peu précises. Dans les études présentées il a été impossible d'utiliser la méthode d'étalon intérieur, car l'addition d'une troisième substance pourrait influencer les interactions intermoléculaires. De même la comparaison avec l'intensité d'une raie de mercure n'est pas satisfaisante, car dans les spectres des solutions de différentes concentra-

tions son intensité n'est pas constante. Cette observation faite au cours de ce travail n'est pas étonnante, car l'intensité des raies de Rayleigh dépend de plusieurs facteurs qui n'ont pas la même valeur dans toutes les solutions étudiées. Pour cette raison on a pu suivre seulement les changements d'intensité des raies les plus intenses en fonction de la concentration. En particulier on a étudié l'intensité des raies de fréquences 989 et 1029 K de la pyridine pure et celle de la raie nouvelle de fréquence 1003 K. Ces trois raies forment une bande commune.

Les spectres ont été photographiés à l'aide d'un spectrographe Huet B II. La concentration des solutions a été la même, qu'auparavant à savoir: 100, 91,5, 80,8, 73,2, 61,0, 48,3, 43,3, 39,8, 37,8, 30,4, 22,3, 21,6, 14,6 et 6,5% mole de pyridine. La fente du spectrographe a été élargie jusqu'à 3,5 K. À cette largeur de la fente on a obtenu des raies suffisamment fortes et en même temps suffisamment fines pour séparer les trois raies formant la bande. À l'aide d'un microphotomètre enregistreur de Moll on a obtenu des courbes photométriques. Pour séparer les trois raies on a recalculé ces courbes en diagrammes d'intensité à l'aide des courbes caractéristiques pour chaque plaque. En supposant, que les raies composantes ont une forme symétrique on a pu facilement les tracer. Elles sont indiquées sur la fig. 1 par pointillés. Les aires limitées par ces courbes sont proportionnelles à l'intensité intégrale.

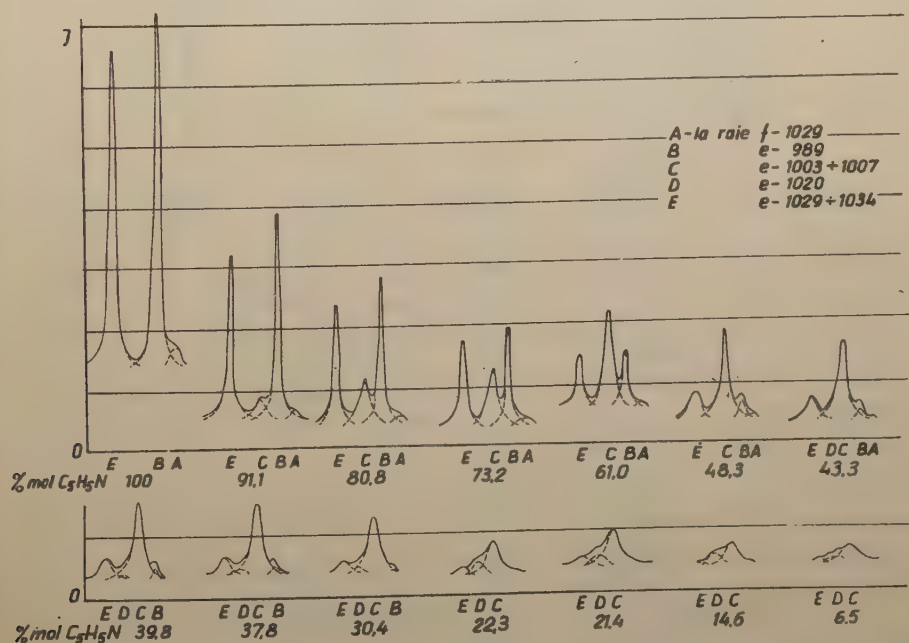


Fig. 1. Contours d'intensité de la bande dans la région de 1000 K dans les spectres des solutions de la pyridine et de l'acide acétique de différentes concentrations d'après la plaque No 58.

III. Résultats

Les résultats des mesures de fréquence des raies dans les spectres des solutions équimolaires de la pyridine sont indiqués au tableau 1. Ces résultats sont représentés également sous la forme d'un diagramme (fig. 2).

Tableau I

Fréquences des raies dans les spectres des solutions équimolaires de la pyridine (en K)

solvent pyridine pure*	HCOOH	CH ₃ COOH*	n-C ₅ H ₇ COOH
601 w	601 vw	601 vw	602 wv
—	—	628 vw	—
650 s	648 m	650 m	650 m
—	696 w	—	—
—	—	—	861 w
888 w	—	880 m	887 w
989 vs	—	990 w	989 w
—	1008 vs	1003 vs	1003 s
1029 vs	1029 m	1030 m	1029 m
1215 m	1215 m	1213 vw	1214 w
1573 m	1576 w	1574 w	1573 w
1580 m	1597 w	1596 w	1596 w
1596 w	—	—	—
3055 vs	3067 m	3068 s	3067 m

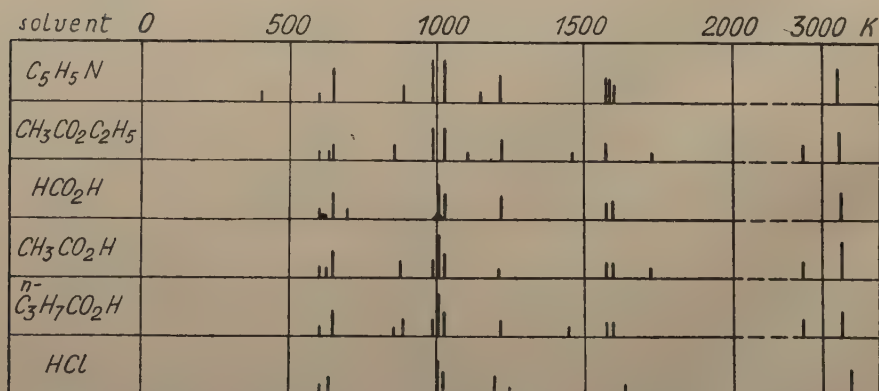


Fig. 2. Diagrammes des spectres des solutions équimolaires de pyridine.

* D'après Mierzecki (1955 a, b)

(vs — très forte, s — forte, m — moyenne, w — faible, vw — très faible).

Le tableau 2 compare les fréquences des raies Raman de la 2,6-lutidine obtenue par différents auteurs. Le tableau 3 et la figure 3 montrent les fréquences des raies dans les spectres des solutions équimolaires de la 2,6-lutidine.

Les résultats des mesures de fréquence des raies dans les solutions deshydratées de la pyridine dans l'acide formique sont indiqués au tableau 4.

Les valeurs relatives de l'intensité intégrale des raies 989, 1003 et 1029 K dans les spectres des solutions de la pyridine et de l'acide acétique d'après trois plaques sont représentées sur la figure 4 a b c. Pour toutes les plaques on a admis l'intensité de la raie nouvelle dans la solution contenant 48% mole de pyridine égale à 100. Les résultats sont précis à 25% près.

On a introduit des corrections pour l'influence du changement de l'indice de réfraction dans les solutions de différentes concentration sur l'intensité mesurée. Suivant Woodward et George (1951) on a multiplié l'intensité mesurée par l'indice de réfraction au carré. En se basant sur les valeurs de l'indice de réfraction pour les

Tableau II

Spectres de la 2,6-lutidine d'après différents auteurs

Manzoni Ansidei (1940)	Herz, Kahovec Kohlrausch (1943)	Travail présent
—	198	197 m
—	210	—
289	288	287 m
—	426	427 vw
515	—	—
534	538	536 m
553	556	553 m
718	717	714 s
801	774	—
—	885	892 vw
996	996	994 vs
1041	—	1038 vw
1092	1093	1092 w
—	1156	1155 vw
1217	—	—
1260	1263	1262 m
—	1277	1274 w
1373	1373	1373 m
—	—	1404 vw
1455	1434	1442 vw
1574	1578	1578 m
1597	1599	1604 vw
2927	2921	2922 s
—	3006	—
3054	3064	3061 m

solutions de la pyridine dans l'acide acétique d'après Pushin et Matavuy (1932) on a construit un diagramme qui représente la variation de l'indice de réfraction en fonction de la concentration. De ce diagramme et du diagramme représentant les

Tableau III

Fréquences des raies dans les spectres des solutions équimolaires de 2,6-lutidine

solvent lutidine pure	HCOOH	CH ₃ COOH	n-C ₃ H ₇ COOH
197 m	207 m	201 m	201 m
287 w	291 w	288 w	291 w
427 vw	—	—	—
536 m	536 m	537 m	538 m
553 m	553 m	554 m	—
—	—	561 w	561 m
714 s	716 m	717 m	719 m
—	—	874 w	864 w
892 vw	—	—	—
994 vs	—	994 w	995 vw
—	1006 s	1008 s	1008 m
1038 vw	—	—	—
1092 w	1095 w	1097 vw	1098 vw
1155 vw	—	1157 vw	1160 vw
1262 m	1268 m	1266 m	1268 m
1274 w	—	—	—
1373 m	1380 w	1378 m	1380 w
1404 vw	—	—	—
1442 vw	—	1441 vw	1450 vw
1578 m	1578 w	1579 w	1580 m
1604 vw	1597 vw	1597 vw	1593 m
2922 s	2927 s	2926 s	2935 s
3061 m	3066 w	3065 m	3068 w

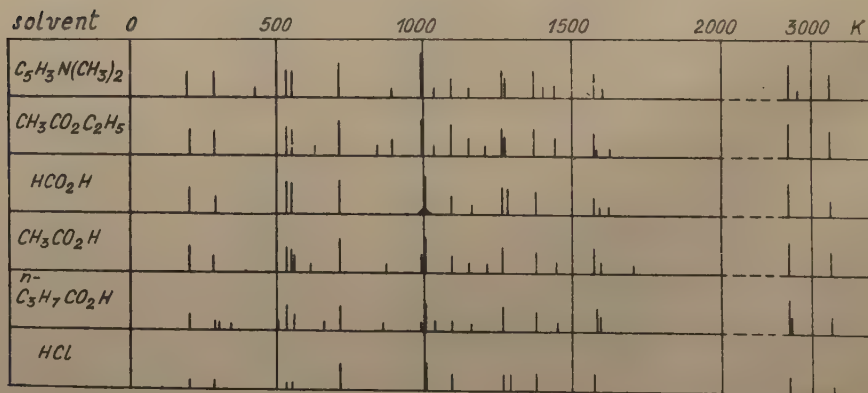


Fig. 3. Diagrammes des spectres des solutions équimolaires de 2,6-lutidine.

Tableau IV

Spectres ramanien des solutions de la pyridine et de l'acide formique à concentration de pyridine inférieure à l'équimolaire

acide formique*	7% mole	9% mole	20% mole	35% mole	pyridine pure**
190 w	224 vw	221 vw	221 vw	221 vw	—
—	611 w	611 w	610 w	—	601 w
—	639 w	639 w	639 w	642 s	—
—	—	—	—	651 m	650 s
679 m	680 m	680 m	680 m	—	—
695 w	701 m	703 m	701 m	696 w	—
—	—	—	—	994 vw	989 vs
—	1011 vs	1011 vs	1011 vs	1010 vs	—
—	—	—	—	1022 m	—
—	1029 w	1029 w	1028 w	1033 sh	1029 vs
1048 w	1061 w	1061 w	1062 w	1063 w	—
1205 m	1205 m	1205 m	1205 m	1208 m	—
—	—	—	1253 w	1254 w	1215 m
1345 vw	1345 w	1348 w	1349 w	1347 w	—
1395 s	1398 s	1398 s	1399 s	—	—
—	—	—	—	1578 w	1573 m
—	—	—	—	—	1580 m
—	—	1604 vw	1604 vw	1604 w	1596 w
—	—	1640 m	1640 m	1636 m	—
1670 s	1672 s	1680 s	1680 s	—	—
—	—	1716 s	1719 s	1714 w	—
1725 m	1734 s	1730 s	—	1740 w	—
2961 vs	2956 vs	2952 vs	2939 vs	2912 s	—
—	—	—	—	3072 vs	3055 s
—	3105 vw	3100 vw	3091 vw	3094 m	—
—	—	—	3107 vw	—	—

valeurs de l'intensité intégrale mesurée (fig. 4 b) on a pris les valeurs pour les solutions contenant 100, 90, 80, 70, 65, 60, 55, 50, 45, 40, 30, 20, et 10% mole de pyridine et on a calculé les valeurs corrigées de l'intensité intégrale (fig. 5).

IV. Discussion

Dans les spectres ramanien des solutions de la pyridine et de l'acide acétique on observe des changements de fréquence qui dépendent de la concentration de la pyridine, ainsi que l'apparition de raies nouvelles absentes dans les spectres des substances pures. On observe en particulier des raies nouvelles de fréquence 628, 1003, et 3068,5 K parallèlement à la disparition partielle des raies 604, 989 et 3055 K de la

* D'après Chiorboli (1957).

** D'après Mierzecki (1955a).

pyridine pure. Ces dernières correspondent alternativement aux oscillations 6 a, 1 et 2 (Kline, Turkevich 1944, Corrins et coll. 1953) (fig. 6). On observe aussi des changements dans la région 1600 K. Dans les spectres des solutions équimolaires de la pyridine dans d'autres acides saturés on observe des changements analogues (Lakshmanan 1954, Mierzecki 1957, Chiorboli 1957, Schwab et Glatzer 1957).

a) Changements dans la région de 1000 K.

L'apparition d'une raie nouvelle dans cette région a été observée dans les spectres des solutions de la pyridine dans différents solvants. Les fréquences de ces raies pour les solutions équimolaires sont indiquées au tableau 5.

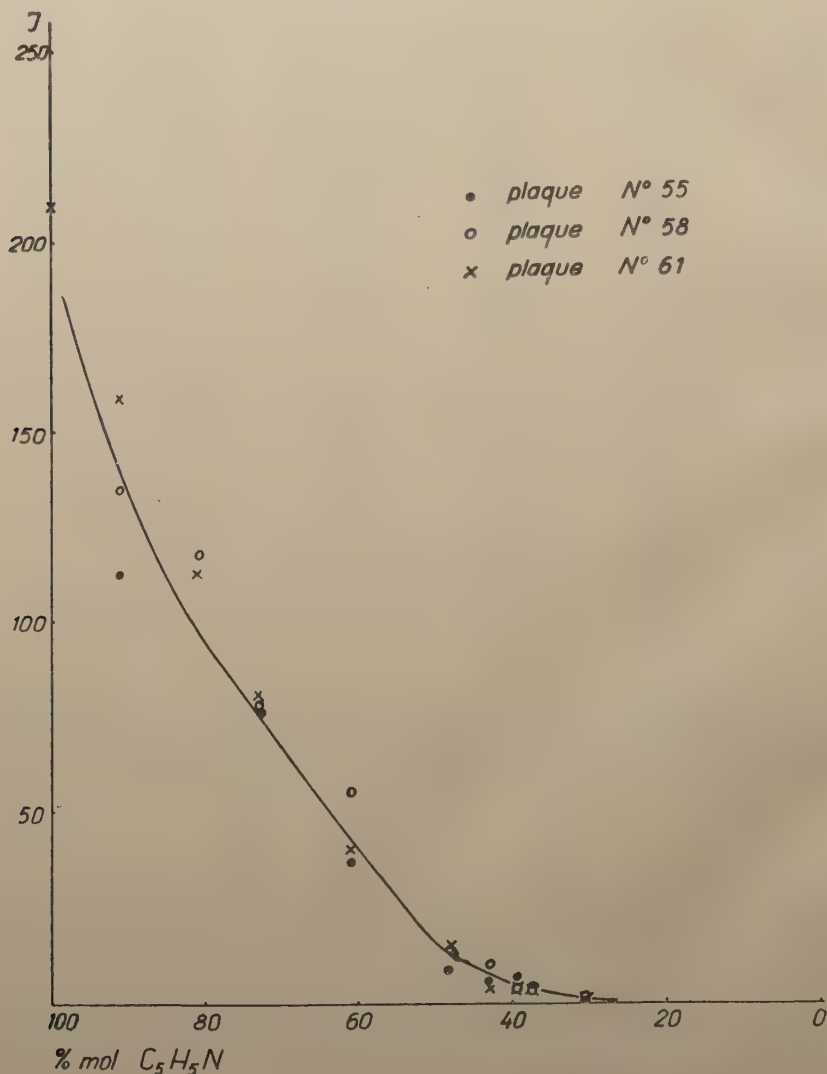


Fig. 4a

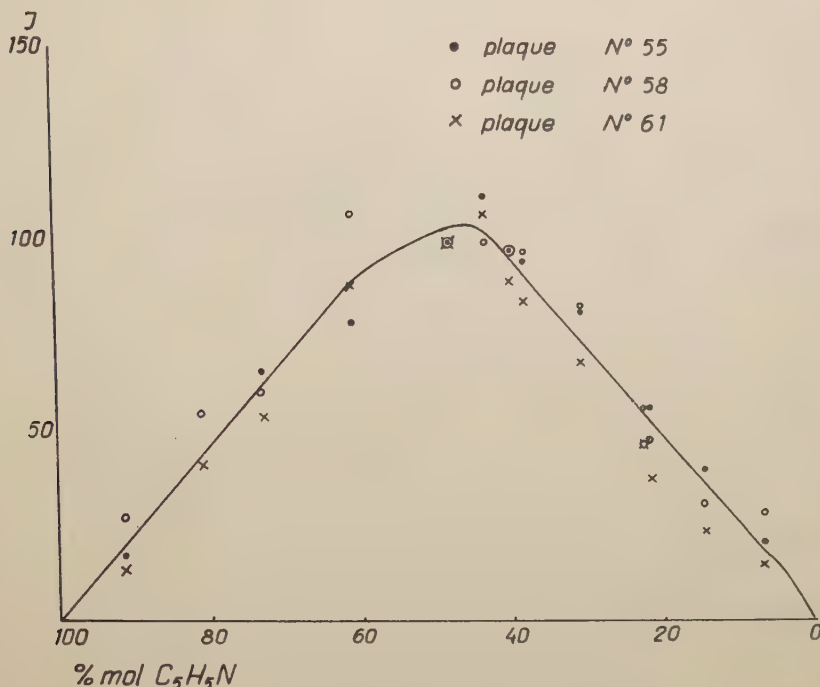


Fig. 4b

Différents auteurs ont observé dans les spectres des solutions aqueuses de la pyridine la raie de fréquence 998 K au lieu de la raie 989 K de la pyridine pure. Les changements des courbes photométriques pour les spectres des solutions aqueuses contenant 79 et 66,5% mole de pyridine (fig. 7) montrent, que, en pleine analogie avec les autres spectres discutés, la raie 998 K existe en outre de la raie 989 K de la pyridine pure et que leurs intensités relatives dépendent de la concentration de la pyridine (Mierzecki 1957). Un phénomène analogue a été observé aussi par Chiorboli (1957).

En comparant les fréquences du tableau 5 on peut remarquer, que 1) La différence entre la fréquence de la raie de la pyridine pure 989 K et la fréquence de la raie nouvelle de la solution ne dépend pas de la masse de la molécule du solvant et que 2) la raie nouvelle apparaît quand la molécule du solvant contient l'hydrogène actif, ainsi que lorsque la molécule du solvant peut former des liaisons de coordination (Tramer 1958).

Dans les spectres des solutions de la pyridine dans l'éther éthylique de l'acide acétique on n'observe aucuns changements dans cette région (fig. 2). La molécule de l'éther ne contient pas d'hydrogène actif et ne peut former de liaisons de coordination.

L'apparition de raies nouvelles dans cette région a été expliquée comme la conséquence de la formation de complexes entre les molécules de la pyridine et celles du

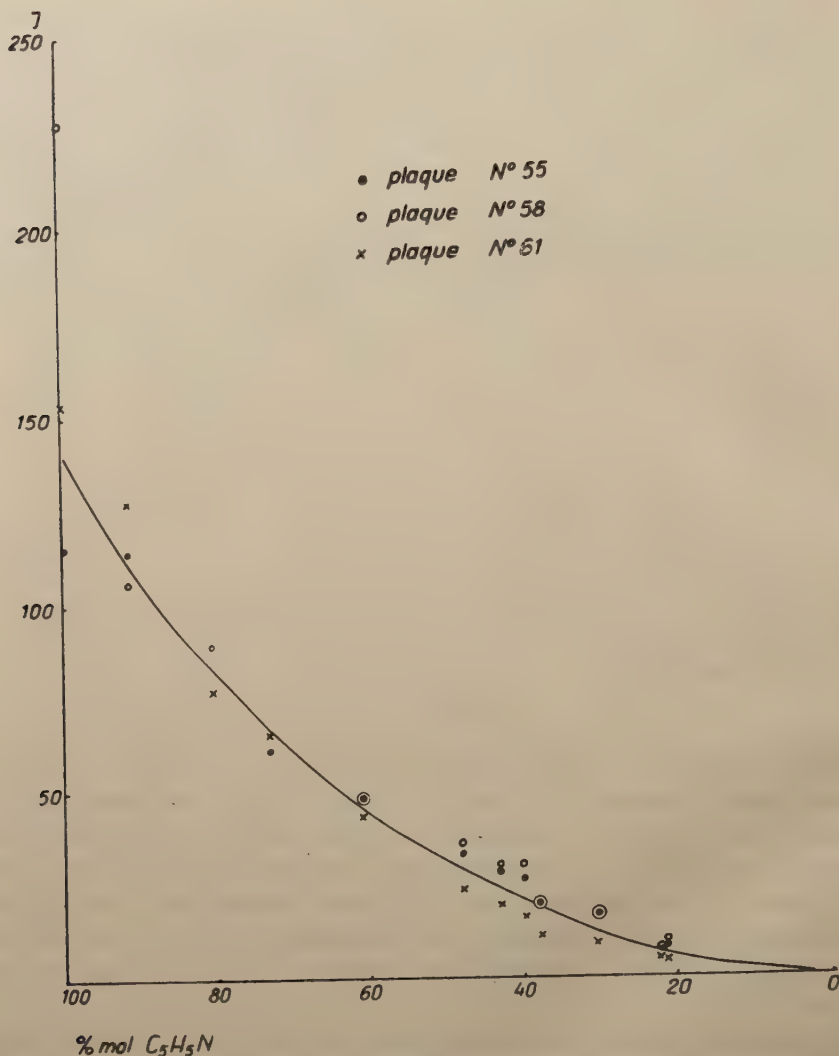


Fig. 4c

Fig. 4. Intensités intégrales des raies a) 989 K, b) 1003 K, c) 1029 K en fonction de la concentration dans les spectres des solutions de pyridine dans l'acide acétique.

solvent. Parmi les différents facteurs pouvant donner comme effet des changements de fréquence on peut considérer les suivants: 1) Alourdissement de l'oscillateur (dans ce cas la fréquence doit être abaissée suivant la masse), 2) le couplage des oscillations de la molécule avec celles de la liaison intermoléculaire (théoriquement on attend l'augmentation ainsi que la diminution de la fréquence et on n'observe que la diminution), 3) les changements structuraux. Le fait que la raie correspondant aux pulsations du

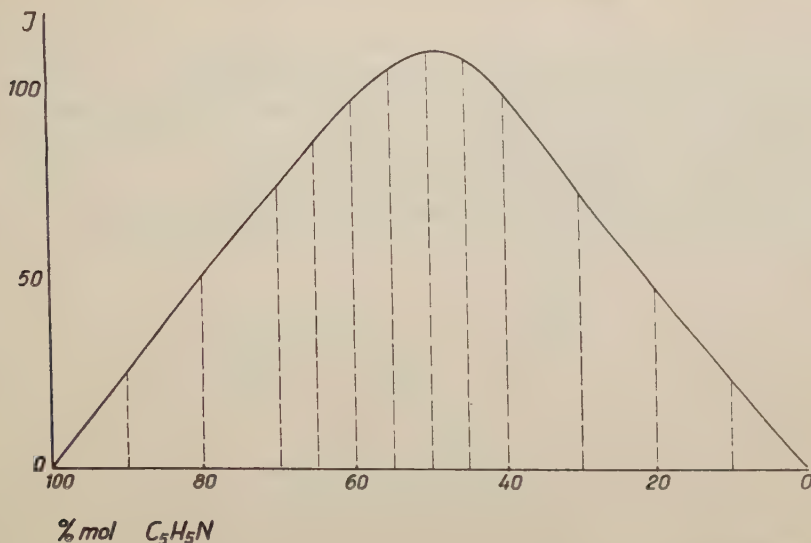


Fig. 5. Intensités intégrales corrigées de la raie 1003 K en fonction de la concentration.

Tableau V

Fréquences des raies nouvelles dans la région de 1000 K. dans les spectres des solutions équimolaires de la pyridine

Solvant	Formule	Fréquence	Auteur
Alcool éthylique	C_2H_5OH	995 ¹	Chiorboli (1957)
Eau	H_2O	996	Krishnamurti (1931)
			Bayard (1943)
			Chiorboli (1957)
Pyrole	C_4H_4N	998	Chiorboli, Manaresi (1954)
Chlorphenol	$OH \cdot C_6H_4 \cdot Cl$	1000	Chiorboli (1957)
acide n-butyrique	C_3H_7COOH	1003	Mierzecki (1957)
acide acétique	CH_3COOH	1003	Mierzecki (1955a)
acide formique	$HCOOH$	1008	Mierzecki (1957)
Chlorure d'antimoine	$SbCl_3$	1000 ²	Tramer (1958)
dioxyd du soufre	SO_2	1006	Tramer (1956)
nitrate d'argent	$AgNO_3$	1006 ³	Tramer (1958)
chlorure d'arsène	$AsCl_3$	1015 ⁴	Tramer (1958)
iod	I_2	1005	(infrarouge) Rice, Walsh (1952)
			Mulliken et coll. (1953)

¹ Cette raie a été observée pour la première fois par Hatem, Valladas-Dubois, Volkinger (1949). D'après nos mesures les résultats de l'auteur italien sont plus précis.

² Concerne la solution — 25% mole du solvant.

³ Concerne la solution concentrée du complexe dans la pyridine (15% mole du solvant). La fréquence dépend de la concentration.

⁴ Concerne la solution — 60% mole du solvant. D'après Tramer (1958) cette raie correspond à un complexe équimolaire. On a observé aussi une raie de fréquence 1000 K qui probablement correspond à un complexe d'une autre composition.

noyau dans les molécules de pyridine qui forment les complexes a une fréquence plus élevée que celle de la pyridine pure doit être alors expliqué par les changements structuraux des molécules de pyridine. Il n'y a aucune raison pour admettre, que les angles du noyau sont changés dans le complexe, car la liaison intermoléculaire est

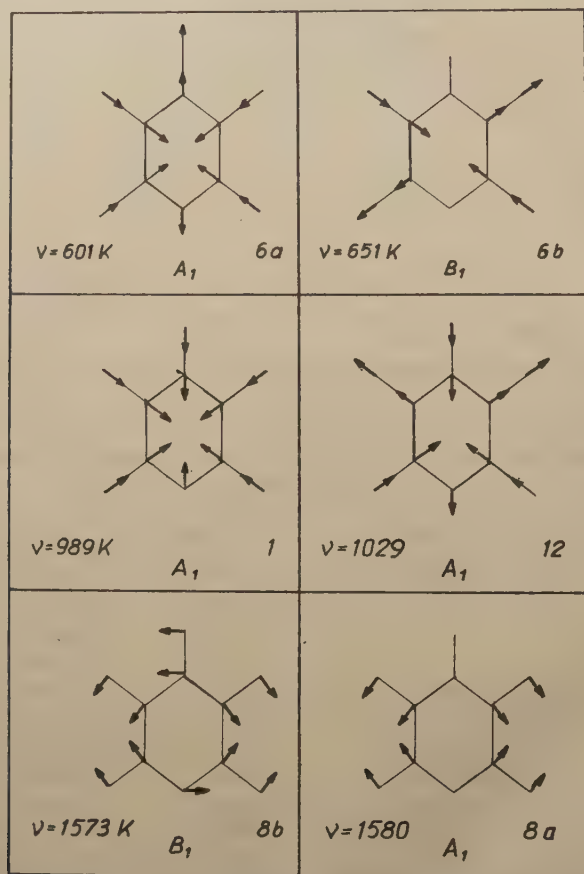


Fig. 6. Oscillations du noyau pyridinique correspondant aux raies discutées.

formée par l'azote qui a une paire d'électrons libres. L'hybridation de cet atome sp^2 est alors la même dans la molécule libre et dans le complexe.

La fréquence plus élevée des raies discutées a été expliquée comme l'effet des changements de distribution de la densité électronique dans la molécule de la pyridine (Mierzecki 1957). Cette distribution influence les constantes de force des liaisons et ceteris paribus — les fréquences. Ces changements sont provoqués par le caractère électrophile de la molécule du solvant et ne dépendent pas de la présence de l'atome de l'hydrogène dans la molécule.

En comparant les résultats des mesures de l'intensité des raies 989 et 1029 K

(fig. 4a et 4c) on observe que l'intensité de la première raie diminue plus vite que celle de la seconde. La raie 989 K disparaît dans les spectres des solutions contenant moins de 25% mole de pyridine, tandis qu'on observe la raie 1029 même dans les spectres des solutions très diluées de la pyridine. Sur cette différence entre les raies du doublet pyridinique on a basé la supposition concernant l'origine de la raie 1003 K. On a supposé, que cette raie est une raie du complexe et qu'elle forme une modification de la raie 989 K (Mierzecki 1957). On ne voit aucune raison d'interpréter cette raie

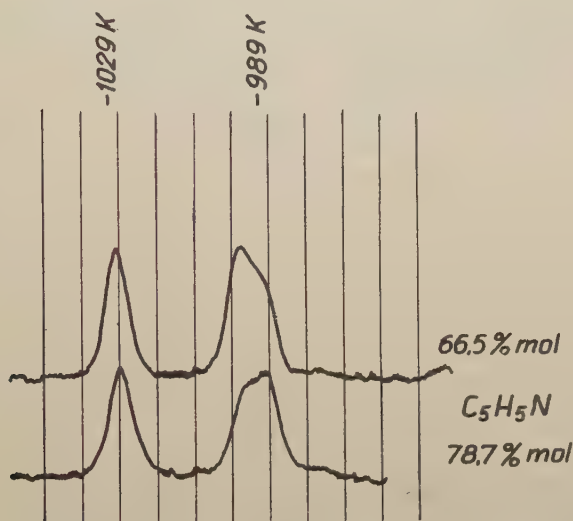


Fig. 7. Courbes photométriques pour la région de 1000 K des spectres des solutions aqueuses de la pyridine.

comme la modification de la raie 1029 K. À notre avis la molécule de pyridine pure effectue des oscillation d'autres fréquences, que la molécule de pyridine formant un complexe. Évidemment une seule molécule n'effectue pas en même temps les oscillations normales d'une molécule de la pyridine pure et celles d'une molécule en complexe (Schwab et Glatzer 1957).

L'intensité de la raie 1003 K passe par un maximum pour la solution équimolaire (fig. 5) (Mierzecki 1956). Ce résultat a été confirmé par Schwab et Glatzer (1957).

Dans les spectres des solutions équimolaires de 2,6-lutidine on observe dans cette région une raie nouvelle de fréquence 1007 K environ en outre de la raie de la substance pure de fréquence 994 K.

b) La raie 1020 K.

Dans la région discutée on observe encore une raie nouvelle de fréquence 1020 K. Dans les travaux précédants on a considéré les trois hypothèses concernant l'origine de cette raie à savoir:

On a supposé que 1) c'est une raie de l'acide acétique renforcée dans les spectres des solutions (Fénéant 1954), 2) que son apparition peut être liée avec l'existence des

ions $C_5H_5NH^+$, ou bien 3) qu'un autre complexe donne origine à cette raie (Mierzecki 1955a, 1956).

Afin d'expliquer l'origine de cette raie on a étudié les spectres des solutions spécialement deshydratées de la pyridine dans l'acide formique à basse concentration de pyridine. Les résultats des mesures de fréquence sont introduits dans le tableau 4. Dans les spectres des solutions contenant 7,9 et 20% mole de pyridine on n'observe dans cette région qu'une seule raie nouvelle de fréquence 1010 K. La raie 1022 K n'a été observée que dans le spectre de la solution composée de 35% mole de pyridine. On a soupçonné que malgré nos précautions cette solution contenait des traces d'eau. Ce soupçon a été confirmé après avoir comparé les spectres des solutions auxquelles

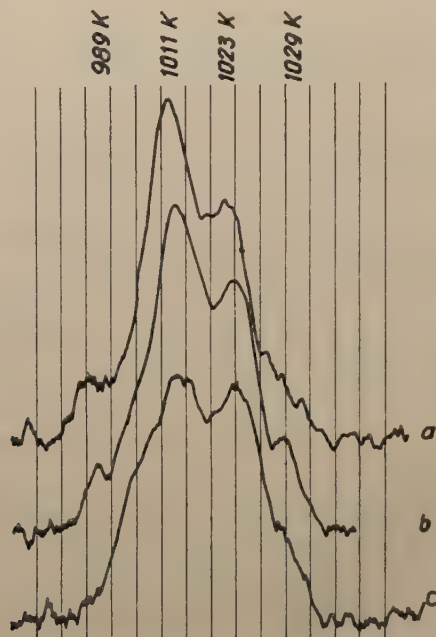


Fig. 8. Influence de l'eau ajoutée à la solution de la pyridine dans l'acide formique contenant 35% mole de pyridine, a) traces d'eau, b) 20% mole d'eau, c) 50% mole d'eau.

on a ajouté de différentes quantités d'eau. Comme le montrent les variations des courbes photométriques sur la figure 8, le rapport de l'intensité de la raie de fréquence 1020 K à celle de la raie de fréquence 1010 K augmente à mesure qu'on ajoute de l'eau à cette solution.

La raie de fréquence 1020 K n'est pas alors une raie d'acide, car dans le spectre de l'acide formique il n'existe aucune raie dans la région de 1000 K. Elle présente une modification d'une des raies de la pyridine. L'apparition de cette raie dépend de la présence de l'eau dans la solution. Cette raie pouvait être observée aussi dans les

spectres des solutions plus diluées de la pyridine dans l'acide formique, quand on a ajouté une quantité suffisante d'eau.

c) La région de 1600 K.

Dans la région de 1600 K on observe les variations suivantes: Dans le spectre de la pyridine pure on observe deux raies assez fortes de fréquence 1573 et 1580 K et une raie faible de fréquence 1596 K. La raie 1573 K correspond à l'oscillation 8b de la symétrie B_1 (Kline, Turkevich 1944, Correns et coll. 1953), la raie 1580 K — à l'oscillation 8a de la symétrie A_1 , la raie 1596 K — à l'oscillation qui est la somme des oscillations 6a et 1 de la symétrie A_1 des fréquences 601 et 989 K. Cette dernière raie est renforcée par la résonance de Fermi avec la raie correspondant à l'oscillation 8a. On peut alors supposer, que sans résonance de Fermi la fréquence de la raie 1580 K serait un peu plus élevée. Dans les spectres des solutions on observe deux raies d'une intensité égale de fréquences 1575 et 1596 K. Cet effet peut être expliqué de la manière suivante (Mierzecki 1957):

La fréquence de la raie correspondant à l'oscillation 1 est plus élevée dans les molécules de la pyridine qui forment des complexes. Les conditions qui permettent la résonance de Fermi n'existent plus. La raie de fréquence 1596 observée dans le spectre de la pyridine pure et dans les spectres des solutions ne correspond pas dans ces deux cas aux mêmes oscillations. Dans le spectre de la pyridine elle correspond à la somme des oscillations 6a et 1, dans les spectres des solutions — à l'oscillation 8a d'une fréquence plus élevée. Des observations et explications analogues ont été dernièrement publiées par Chiorboli (1957).

Dans les spectres des solutions de 2,6-lutidine on n'observe pas de variations analogues dans cette région, car dans le spectre de la lutidine la résonance de Fermi n'existe plus.

d) la région de 3000 K.

Dans les spectres des solutions de la pyridine dans les acides saturés on observe dans cette région une raie nouvelle de fréquence 3068 K environ. Comme on a montré dans le travail précédant (Mierzecki 1955a) cette raie apparaît en plus de la raie 3055 K de la pyridine. Dans les spectres des solutions plus diluées de la pyridine dans l'acide formique on observe encore une autre raie nouvelle de fréquence 3096 K environ. Cette raie devient plus forte, quand on ajoute de l'eau à la solution contenant 35% mole de pyridine. Elle est observée comme une seule raie dans cette région dans les spectres des solutions deshydratées plus diluées avec l'acide formique. Cette raie a été observée par Chiorboli (1957) dans les spectres des solutions de la pyridine dans les acides acétique et formique à basse concentration de la base.

Dans les solutions équimolaires de 2,6-lutidine on observe dans cette région une raie de fréquence 3067 K environ, un peu plus élevée en comparaison avec la raie de la base pure 3061 K.

La raie de fréquence 3055 K dans le spectre de la pyridine correspond à l'oscillation plane symétrique des liaisons C—H. Le changement de cette fréquence dans les spectres des solutions peut être expliqué comme l'effet du changement de la distri-

bution électronique dans toute la molécule de la pyridine, les liaisons C—H comprises. D'après Chiorboli (1957) la raie de fréquence 3096 K correspond aux oscillations des liaisons C—H dans les molécules ioniques de la pyridine.

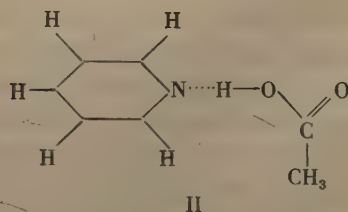
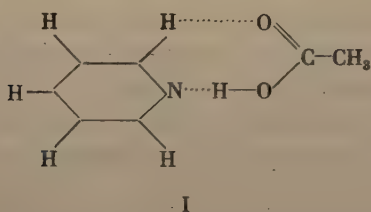
V. Conclusions

Dans les spectres des solutions des bases pyridiniques dans les acides saturés on observe l'apparition de raies nouvelles en plus des raies des bases pures. En particulier on observe des raies nouvelles dans la région de 1000 K et dans la région de 3000 K.

En se basant sur les mesures d'intensité de la raie nouvelle de 1003 K et des raies de la pyridine 989 et 1029 K dans les spectres des solutions de cette base dans l'acide acétique en fonction de la concentration on peut conclure, que 1) la raie 1003 K présente une modification de la raie 989 K et que 2) le complexe qui se forme dans les solutions étudiées et qui est responsable de l'apparition de cette raie, est composé d'un nombre égal de molécules de la base et de l'acide et probablement contient une molécule de chaque substance (Mierzecki 1956, 1957). Lakshmanan (1954) et Chiorboli (1957) qui n'ont pas mesuré l'intensité de cette raie donnent d'autres formules pour le complexe. Il semble, que leurs résultats ne donnent pas de preuves suffisantes à leurs conclusion.

Dans les spectres des solutions étudiées à haute concentration de pyridine on observe la raie de fréquence 1720 K (Mierzecki 1955 b). Une raie analogue a été observée aussi par Chiorboli (1957). D'après l'auteur italien cette raie doit être liée avec les oscillations de la liaison C = O de la molécule de l'acide prenant part à une liaison d'hydrogène. C'est pour cette raison, qu'il suggère, que le complexe se compose d'une molécule de pyridine et de deux molécules d'acide.

Syrkin et Sobczyk (1956) qui ont étudié les moments dipolaires des solutions discutées proposent pour le complexe une formule I, d'après laquelle une seconde liaison d'hydrogène peut se former entre le groupe C = O de l'acide et le groupe C—H en position 2 du noyau pyridinique. Un noyau du chelat qui se forme ainsi, doit stabiliser cette formule. On pourrait expliquer par cette formule l'apparition de la raie 1720 K au lieu de la raie 1745 K caractéristique pour la liaison C = O libre.



On peut d'autre part expliquer l'apparition de cette raie par l'influence de changement de la distribution de la densité électronique dans toute la molécule de l'acide.

Par le même effet on peut expliquer aussi, que la raie qui correspond aux oscillations de la liaison C—C dans la molécule de l'acide acétique est déplacée à une fréquence plus élevée (Mierzecki 1953, 1955b, 1957, Chiorboli 1957). Dans ce cas la formule II peut représenter la structure du complexe.

On a montré, que l'apparition de la raie 1020 K dépend de la présence de l'eau dans les solutions. Les solutions dans les spectres desquelles on l'avait observée n'étaient pas probablement deshydratées d'une manière suffisante. Il est bien possible, que des complexes triples composés des molécules de la base, de l'acide et de l'eau sont à l'origine de cette raie.

L'auteur tient à exprimer à MM. les Professeurs dr J. Pniewski et dr T. Skaliński les remerciements les plus sincères pour l'intérêt qu'ils ont porté à ce travail.

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ON THE THEORY OF MAGNETIC ANISOTROPY OF FERROMAGNETIC CRYSTALS

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Using the second quantization method of Holstein-Primakoff and Tiablikov, the author has calculated:

1. the magnetic field value and direction dependence of energy of crystals with no spin waves excitation, 2. the magnetic field value and direction dependence of dispersion formulae, 3. the temperature and magnetic field value and direction dependence of free energy and of crystal magnetic anisotropy constants. These calculations were performed for simple, body centered and face centered cubic lattices as well as for simple hexagonal and closely packed hexagonal lattices.

1. Introduction

Ferromagnetic single crystals show anisotropy of magnetic properties. The free energy of ferromagnetic single crystals is a function of the angles between the direction of spontaneous magnetization and the crystal axes and the direction of external magnetic field.

In the following calculations we shall neglect the spontaneous magnetostriction and all external tensions. The anisotropic part of free energy will be then determined by the crystallographical symmetry of lattice.

This part of energy we will call the magnetocrystalline anisotropic energy.

Akulov (1929) has indirectly defined the so called tensor of ferromagnetic anisotropy using the symmetry properties of cubic crystals. This tensor permits to find the formula for the anisotropic magnetocrystalline energy:

$$F = K_0 + K_1 \omega + K_2 \alpha_1^2 \alpha_2^2 \alpha_3^2, \quad (1)$$

$$\omega = \alpha_1^2 \alpha_2^2 + \alpha_1^2 \alpha_3^2 + \alpha_2^2 \alpha_3^2,$$

where α_i are cosines of the angles between the vector of spontaneous magnetization and the crystal axes, and K_1, K_2 the so called anisotropy constants. The formula (1) can be obtained also by means of rather simple symmetry considerations (Vonsovski, Shur 1948).

By means of the tensor of ferromagnetic anisotropy we can treat all the fundamental problems of the theory of technical magnetization for magnetic fields causing rotation of the spontaneous magnetization.

On the basis of classical theories we cannot explain the dependence of the anisotropy constants upon magnetic field and temperature.

In the paper quoted above Akulov has shown that the magnetocrystalline anisotropy is caused by magnetic coupling.

Strictly considered, the magnetic interactions are relativistic effects. Unfortunately, the relativistic quantum mechanics of many particles is not yet sufficiently developed and therefore we have to introduce the magnetic part of energy on the basis of correspondence considerations.

The magnetic energy is very small in comparison with the exchange energy. Nevertheless, the magnetic energy represents a dominant factor for the phenomena of technical magnetization. This is caused by the fact that changes of energy of lattice stationary states, which correspond to isotropic interactions of atoms, and are caused by the magnetic interaction energy, are large in comparison with the differences of energy for the nonperturbed lattice states.

Many authors have calculated the influence of magnetic interactions by means of the usual perturbation theory. This procedure is incorrect because, as mentioned above, the changes of energy levels caused by magnetic perturbation are not small in comparison with the differences of unperturbed levels.

To overcome this difficulty one can introduce a very strong external magnetic field, so as to enlarge the differences between the neighbouring energy levels of lattice. This has the drawback that one can not investigate then the dependence of free energy on the magnetic field direction, because in a very strong magnetic field the resultant magnetization is directed always along the magnetic field.

The correct calculation of anisotropic free energy can be performed by the methods elaborated by Bogoliubov and Tiablikov (1949) or by Holstein and Primakoff (1940).

One has to remark (Vonsovski et alii 1955) that the magnetic energy consists of a quasiclassical part (Holstein, Primakoff 1940) and an exchange part (Tiablikov 1950).

In this paper we shall neglect quasiclassical multipole interactions (the long range interactions) because, these interactions do not play any larger part in the problem of magnetic anisotropy.

The magnetic exchange energy is caused by not radially symmetric shape of electron-clouds at the lattice nodes. In the electrostatic field of ions the electron-clouds orientate themselves with regard to the crystallographical axes. The magnetic spin moments „feel” the symmetry of crystallographical lattice owing to their interactions with orbital magnetic moments.

For the following calculations we take into account only the dipole-dipole and quadrupole-quadrupole magnetic exchange coupling.

We shall proceed to calculate the anisotropic part of free energy of ferromagnetic

single crystal with hexagonal and cubic structure, and we shall obtain the temperature dependence of anisotropy constants, as well as their dependence on values and direction of magnetic field with regard to crystallographical axes.

2. The Hamilton Operator

We assume that the crystal consists of magnetic ions, each with a resultant spin S . For simplicity we shall omit the interactions of magnons with magnons and with phonons.

It is convenient to perform the calculations in the spin space because, from the polar theory of metals (Bogoliubov 1949), for spin excitations only, the Dirac — Hamiltonian results for each spin value. Therefore in my paper the Hamiltonian is following (Van Vleck 1937, Holstein and Primakoff 1940):

$$\hat{\mathcal{H}} = -\frac{1}{2} \sum_{l \neq m}^N 2J(R_{lm}) \hat{S}_l \cdot \hat{S}_m + \frac{1}{2} \sum_{l \neq m} P(R_{lm}) [\hat{S}_l \cdot \hat{S}_m - 3(\hat{S}_l \cdot \vec{R}_{lm})(\hat{S}_m \cdot \vec{R}_{lm}) R_{lm}^{-2}] + \\ + \frac{1}{2} \sum_{l \neq m} Q(R_{lm}) (\hat{S}_l \cdot \vec{R}_{lm})^2 (\hat{S}_m \cdot \vec{R}_{lm})^2 R_{lm}^{-4} - \mu \sum_{l=1}^N \vec{H} \cdot \hat{S}_l, \quad (2)$$

In the expression above

$J(R_{lm})$ stands for the exchange integral between l -th and m -th atoms;

R_{lm} for the distance between l -th and m -th atoms;

$P(R_{lm})$ for the coefficient of magnetic pseudodipolar or "anisotropic exchange" coupling, whose approximate value is $\sim J(R_{lm}) \cdot (g-2)^2$ (Van Vleck 1956);

$Q(R_{lm})$ for the coefficient of magnetic pseudoquadrupolar or "anisotropic exchange" coupling whose approximate value is $\sim 1/4 J(R_{lm}) \cdot (g-2)^4$;

g for the Landé-factor, supposed isotropic;

\hat{S}_l for the spin operator of the l -ions in $\hbar/2$ units;

\vec{H} for the external magnetic field;

μ for the value of Bohr-magneton;

N for the total number of atoms.

3. Eigenvalues of the Hamiltonian

It is convenient to introduce instead of spin-operators the Bose operators \hat{b}_l, \hat{b}_l^* (see Appendix I) by means of relations:

$$\hat{S}_l^z = S_l^z \left(1 - 2 \frac{\hat{n}_l}{S_l}\right) + \Omega_l^z \cdot f(\hat{n}_l) \hat{b}_l + \Omega_l^{z*} \hat{b}_l^* f(\hat{n}_l), \\ \hat{n}_l = \hat{b}_l^* \hat{b}_l, \\ f(\hat{n}_l) = \left(1 - \frac{\hat{n}_l}{S_l}\right)^{\frac{1}{2}}, \quad (3)$$

Here

S_l^a are the a components of c -spin-vectors of length S_l , \hat{b}_l^* , \hat{b}_l stand for the creation v. z. annihilation operators.

The S_l^a satisfy the relations:

$$\sum_a (S_l^a)^2 = S_l^2, \quad l = 1, 2, \dots, N, \quad (4)$$

$\vec{\Omega}_l$ vectors are defined by formulae:

$$\begin{aligned} \Omega_l^x &= \frac{1}{2} S_l^{-1} \cdot [-e^{i\varphi_l} (S_l + S_l^*) + e^{-i\varphi_l} \cdot (S_l - S_l^*)], \\ \Omega_l^y &= \frac{i}{2} \cdot S_l^{-1} [e^{i\varphi_l} \cdot (S_l + S_l^*) + e^{-i\varphi_l} \cdot (S_l - S_l^*)], \\ \Omega_l^z &= S_l^{-1} [S_l^2 - (S_l^*)^2], \\ e^{i\varphi_l} &= (S_l^x + iS_l^y) \cdot [(S_l^x)^2 + (S_l^y)^2]^{-1/2}, \end{aligned} \quad (5)$$

and they satisfy the following relations:

$$\begin{aligned} \vec{\Omega}_l \cdot \vec{\Omega}_l &= \vec{\Omega}_l^* \cdot \vec{\Omega}_l^* = \vec{S}_l \cdot \vec{\Omega}_l = \vec{S}_l^* \cdot \vec{\Omega}_l^* = 0, \quad \vec{\Omega}_l^* \cdot \vec{\Omega}_l = 2S_l, \\ \Omega_l^{x*} \Omega_l^x &= S_l^{-1} \cdot [S_l^2 - (S_l^y)^2], \quad \Omega_l^{y*} \Omega_l^y = S_l^{-1} \cdot [S_l^2 - (S_l^x)^2], \\ \Omega_l^{z*} \Omega_l^z &= S_l^{-1} [S_l^2 - (S_l^x)^2], \end{aligned} \quad (6)$$

When we substitute (3) into (2) we get in the free magnons approximation

$$\hat{\mathcal{H}} = E_0 + \hat{\mathcal{H}}_1 + \hat{\mathcal{H}}_2, \quad (7)$$

where

$$\begin{aligned} E_0 &= -\frac{1}{2} \sum_{l \neq m} 2J(R_{lm}) \vec{S}_l \cdot \vec{S}_m + \frac{1}{2} \sum_{l \neq m} P(R_{lm}) [\vec{S}_l \cdot \vec{S}_m - 3(\vec{S}_l \cdot \vec{R}_{lm})(\vec{S}_m \cdot \vec{R}_{lm}) R_{lm}^{-2}] + \\ &+ \frac{1}{2S^2} \sigma \sum_{l \neq m} Q(R_{lm}) (\vec{S}_l \cdot \vec{R}_{lm})^2 (\vec{S}_m \cdot \vec{R}_{lm})^2 R_{lm}^{-4} + \frac{1}{2} S^2 \sum_{l \neq m} Q(R_{lm}) + \\ &+ (S-1) \sum_{l \neq m} Q(R_{lm}) R_{lm}^{-2} (\vec{S}_l \cdot \vec{R}_{lm})^2 - \mu \sum_{l=1}^N \vec{H} \cdot \vec{S}_l, \end{aligned} \quad (8)$$

$$\sigma = S^2 - 2S + 1,$$

represents the energy of fundamental lattice state in the first approximation.

The zero-th approximation represents the classical Hamiltonian.

$\hat{\mathcal{H}}_1$, $\hat{\mathcal{H}}_2$ are small operators of the first v. z. second order of magnitude with regard to operators \hat{b}_l and \hat{b}_l^* .

We shall calculate \vec{S}_l from the condition of minimum of energy E_0 with additional conditions (4).

We get the following equations:

$$\begin{aligned}
 & - \sum_{l=1}^N 2J(R_{lm}) \vec{S}_l + \sum_{l=1}^N P(R_{lm}) [\vec{S}_l - 3(\vec{S}_l \cdot \vec{R}_{lm}) \vec{R}_{lm} R_{lm}^{-2}] + \\
 & + 2(S-1) \sum_{l=1}^N Q(R_{lm}) (\vec{S}_l \cdot \vec{R}_{lm}) \vec{R}_{lm} R_{lm}^{-2} + \\
 & + \frac{2}{S^2} \sigma \sum_{l=1}^N Q(R_{lm}) (\vec{S}_l \cdot \vec{R}_{lm})^2 (\vec{S}_m \cdot \vec{R}_{lm}) \vec{R}_{lm} R_{lm}^{-4} - \mu \vec{H} = \nu_m \vec{S}_m, \quad (9)
 \end{aligned}$$

where ν_m are the Lagrange factors.

Taking into account the formula (9) we can transform $\hat{\mathcal{H}}_1$ to the form:

$$\hat{\mathcal{H}}_1 = \sum_{m=1}^N \nu_m \vec{S}_m \cdot \vec{\tau}_m, \quad (10)$$

where

$$\tau_l^\alpha = \Omega_l^\alpha \hat{b}_l + \Omega_l^{\alpha*} \hat{b}_l^*. \quad (11)$$

On the basis of conditions (6) we have $\hat{\mathcal{H}}_1 \equiv 0$

The full Hamiltonian has then the form:

$$\begin{aligned}
 \hat{\mathcal{H}} = E_0 + \sum_{l \neq m} A(R_{lm}) \hat{b}_l^* \hat{b}_m + \sum_{l \neq m} B(R_{lm}) \hat{b}_l \hat{b}_l + \sum_{l \neq m} C(R_{lm}) \hat{b}_l^* \hat{b}_m^* + \\
 + \sum_{l \neq m} D(R_{lm}) \hat{b}_l \hat{b}_m + \sum_{l \neq m} E(R_{lm}) \hat{b}_l^* \hat{b}_l^* + \sum_{l \neq m} G(R_{lm}) \hat{b}_l \hat{b}_l, \quad (12)
 \end{aligned}$$

where

$$\begin{aligned}
 A(R_{lm}) &= -4J(R_{lm})S + 4P(R_{lm})S - 6P(R_{lm})(\vec{\Omega}_l^* \cdot \vec{R}_{lm})(\vec{\Omega}_m \cdot \vec{R}_{lm})R_{lm}^{-2} + \\
 & + \frac{4}{S^2} \sigma \cdot Q(R_{lm})(\vec{S}_l \cdot \vec{R}_{lm})(\vec{S}_m \cdot \vec{R}_{lm})(\vec{\Omega}_l^* \cdot \vec{R}_{lm})(\vec{\Omega}_m \cdot \vec{R}_{lm})\vec{R}_{lm}^{-4}, \\
 B(R_{lm}) &= \frac{2}{S^3} (-3S^2 + 3S - 1) Q(R_{lm})(\vec{S}_l \cdot \vec{R}_{lm})^2 (\vec{S}_m \cdot \vec{R}_{lm})^2 R_{lm}^{-4} + 2S^2 Q(R_{lm}) + \\
 & + \frac{2}{S} (-3S + 1) Q(R_{lm})(\vec{S}_l \cdot \vec{R}_{lm})^2 R_{lm}^{-2} + 2(S-1) Q(R_{lm})(\vec{S}_m \cdot \vec{R}_{lm})^2 R_{lm}^{-2}, \\
 C(R_{lm}) &= -\frac{3}{2} P(R_{lm})(\vec{\Omega}_l \cdot \vec{R}_{lm})(\vec{\Omega}_m \cdot \vec{R}_{lm})R_{lm}^{-2} + \\
 & + \frac{2}{S^2} \sigma Q(R_{lm})(\vec{S}_l \cdot \vec{R}_{lm})(\vec{S}_m \cdot \vec{R}_{lm})(\vec{\Omega}_l^* \cdot \vec{R}_{lm})(\vec{\Omega}_m \cdot \vec{R}_{lm})R_{lm}^{-4}, \\
 D(R_{lm}) &= -\frac{3}{2} P(R_{lm})(\vec{\Omega}_l \cdot \vec{R}_{lm})(\vec{\Omega}_m \cdot \vec{R}_{lm})R_{lm}^{-2} + \\
 & + \frac{2}{S^2} \sigma Q(R_{lm})(\vec{S}_l \cdot \vec{R}_{lm})(\vec{S}_m \cdot \vec{R}_{lm})(\vec{\Omega}_l \cdot \vec{R}_{lm})(\vec{\Omega}_m \cdot \vec{R}_{lm})R_{lm}^{-4},
 \end{aligned}$$

$$\begin{aligned}
E(R_{lm}) &= Q(R_{lm}) (\vec{\mathcal{Q}}_l^* \cdot \vec{R}_{lm})^2 (\vec{S}_m \cdot \vec{R}_{lm})^2 R_{lm}^{-4} + \\
&+ Q(R_{lm}) (\vec{\mathcal{Q}}_l^* \cdot \vec{R}_{lm})^2 (\vec{\mathcal{Q}}_m \cdot \vec{R}_{lm}) (\vec{\mathcal{Q}}_m^* \cdot \vec{R}_{lm}) R_{lm}^{-4}, \\
G(R_{lm}) &= Q(R_{lm}) (\vec{\mathcal{Q}}_l \cdot \vec{R}_{lm})^2 (\vec{S}_m \cdot \vec{R}_{lm})^2 R_{lm}^{-4} + \\
&+ Q(R_{lm}) (\vec{\mathcal{Q}}_l \cdot \vec{R}_{lm})^2 (\vec{\mathcal{Q}}_m \cdot \vec{R}_{lm}) (\vec{\mathcal{Q}}_m^* \cdot \vec{R}_{lm}) R_{lm}^{-4}.
\end{aligned} \tag{13}$$

We can transform the Hamiltonian above to diagonal form. For this purpose we shall pass from space-representation to momentum-representation, or, expressing this in another way, from creation (or annihilation) operators for reversed spins to creation (or annihilation) operators for spin waves.

In order to do this, we put

$$\begin{aligned}
\hat{b}_l &= N^{-\frac{1}{2}} \sum_{\lambda} \exp(-i \vec{K}_{\lambda} \cdot \vec{R}_l) \hat{b}_{\lambda}, \\
\hat{b}_l^* &= N^{-\frac{1}{2}} \sum_{\lambda} \exp(i \vec{K}_{\lambda} \cdot \vec{R}_l) \hat{b}_{\lambda}^*,
\end{aligned} \tag{14}$$

where $K_{\lambda}^1 = \frac{2\pi\lambda_x}{G_1}$, $K_{\lambda}^2 = \frac{2\pi\lambda_y}{G_2}$, $K_{\lambda}^3 = \frac{2\pi\lambda_z}{G_3}$, $\lambda_1, \lambda_2, \lambda_3$ assume any integral values between $-\frac{1}{2} G_1$ and $\frac{1}{2} G_1 - 1$, $-\frac{1}{2} G_2$ and $\frac{1}{2} G_2 - 1$, $-\frac{1}{2} G_3$ and $\frac{1}{2} G_3 - 1$, respectively. G_1, G_2 and G_3 are the lengths of the specimen in the 1, 2, 3 directions in units of lattice constant.

Neglecting the influence of boundaries of the specimen, we obtain thus the following form of Hamiltonian:

$$\hat{\mathcal{H}} = E_0 + \sum_{\lambda} U_{\lambda} \hat{b}_{\lambda}^* \hat{b}_{\lambda} + \sum_{\lambda} V_{\lambda}^+ \hat{b}_{\lambda}^* \hat{b}_{-\lambda}^* + \sum_{\lambda} V_{\lambda}^- \hat{b}_{\lambda} \hat{b}_{-\lambda}, \tag{15}$$

where

$$\begin{aligned}
U_{\lambda} &= \sum_{h \neq 0} [A(R_h) \exp(i \vec{K}_{\lambda} \cdot \vec{R}_h) + B(R_h)], \quad \vec{R}_h = \vec{R}_l - \vec{R}_m, \\
V_{\lambda}^+ &= \sum_{h \neq 0} [C(R_h) \exp(i \vec{K}_{\lambda} \cdot \vec{R}_h) + E(R_h)], \\
V_{\lambda}^- &= \sum_{h \neq 0} [D(R_h) \exp(i \vec{K}_{\lambda} \cdot \vec{R}_h) + G(R_h)].
\end{aligned} \tag{16}$$

\sum_h stands for the summation over all the next neighbours of any atoms.

If the magnetic interactions V_{λ}^+ and V_{λ}^- were neglected, the Hamiltonian above would be diagonal. The Hamiltonian (15) is not diagonal, because operators $\hat{b}_{\lambda} \hat{b}_{-\lambda}$ and $\hat{b}_{\lambda}^* \hat{b}_{-\lambda}^*$ do not commute with $\hat{b}_{\lambda} \hat{b}_{\lambda}$.

In order to diagonalize the full Hamiltonian we use the methods of Holstein and Primakoff or Tiablikov (Bogoliubov 1949, p. 206) putting:

$$\begin{aligned}\hat{b}_\lambda &= \frac{1}{\sqrt{2}} \exp(i\varphi_\lambda) [l_1(\hat{c}_\lambda + \hat{c}_{-\lambda}) + l_2(\hat{c}_\lambda^* - \hat{c}_{-\lambda}^*)], \\ \hat{b}_{-\lambda} &= \frac{1}{\sqrt{2}} \exp(i\varphi_{-\lambda}) [l_1(\hat{c}_\lambda - \hat{c}_{-\lambda}) + l_2(\hat{c}_\lambda^* + \hat{c}_{-\lambda}^*)].\end{aligned}\quad (17)$$

We define this transformation for the positive halfspace of \vec{K}_λ only, i. e. we put $\vec{K}_{-\lambda} = -\vec{K}_\lambda$.

We confine our attention to the case of $|\vec{K}_\lambda| \ll 1$, i. e. to the long spin waves. Then

$$l_1 = \left[\frac{1}{2} \frac{U_\lambda + (U_\lambda^2 - |V_\lambda|^2)^{\frac{1}{2}}}{(U_\lambda^2 - |V_\lambda|^2)^{\frac{1}{2}}} \right]^{\frac{1}{2}}, \quad l_2 = \left[\frac{1}{2} \frac{U_\lambda - (U_\lambda^2 - |V_\lambda|^2)^{\frac{1}{2}}}{(U_\lambda^2 - |V_\lambda|^2)^{\frac{1}{2}}} \right]^{\frac{1}{2}}.$$

By use of the formulae (17) we get the following form of the Hamiltonian:

$$\hat{\mathcal{H}} = E_0 + \Delta E + \sum_\lambda E_\lambda \hat{c}_\lambda^* \hat{c}_\lambda, \quad (18)$$

where

$$E_\lambda = (U_\lambda^2 - |V_\lambda|^2)^{\frac{1}{2}}, \quad \Delta E = \frac{1}{2} \sum_\lambda (E_\lambda - U_\lambda), \quad (19)$$

and $\hat{c}_\lambda^*, \hat{c}_\lambda$ are Bose operators.

The eigenvalues of the operators $\hat{c}_\lambda^* \hat{c}_\lambda$ are $n_\lambda = 0, 1, 2, \dots$

4. The Fundamental Energy Levels of the Crystal at 0°K

We assume that the crystal in the lowest energy state is magnetized to saturation, i. e. the \vec{S}_l vectors do not depend upon the l -factors.

The cubic lattices:

$$E_0 = K_0 + K_1 \omega - N\mu \vec{H} \cdot \vec{S}. \quad (20)$$

We get the second anisotropy constant K_2 if we take into account the hexapole interaction.

a. The simple cubic lattice:

$$\begin{aligned}\vec{R}_h &= R_h \vec{r}_h = a \cdot \vec{r}_h, \\ \vec{r}_h &= \pm \vec{e}_x; \pm \vec{e}_y; \pm \vec{e}_z,\end{aligned}$$

a — lattice constant; $\vec{e}_x, \vec{e}_y, \vec{e}_z$ stand for the reciprocally orthogonal unit vectors.

There are six nearest neighbours for each lattice node. In the zero-th approximation ($E_0^{(0)}$) i. e. for the classical Hamilton function we get:

$$K_0 = -6NJS^2 + NQS^4, \quad K_1 = -2NQS^4,$$

In the first approximation ($E_0^{(1)}$) which corresponds to a state with no spin waves:

$$K'_0 = -6NJS^2 + NQS^2(S^2 + 2),$$

$$K'_1 = -2NQS^2\sigma.$$

We get from the conditions (9) for energy minimum the following values for spin-components:

I.

$$\text{for } S^x = 0: \quad S^y = \pm \frac{\sqrt{2}}{2} S, \quad S^z = \pm \frac{\sqrt{2}}{2} S,$$

$$\text{for } S^y = 0: \quad S^x = \pm \frac{\sqrt{2}}{2} S, \quad S^z = \pm \frac{\sqrt{2}}{2} S,$$

$$\text{for } S^z = 0: \quad S^x = \pm \frac{\sqrt{2}}{2} S, \quad S^y = \pm \frac{\sqrt{2}}{2} S.$$

i. e. crystallographic directions of the type $[110]$.

II.

$$\text{for } S^x = S^y = 0: \quad S^z = \pm S,$$

$$\text{for } S^x = S^z = 0: \quad S^y = \pm S,$$

$$\text{for } S^y = S^z = 0: \quad S^x = \pm S.$$

i. e. crystallographic directions of the type $[100]$.

III.

$$\text{for } S^x \cdot S^y \cdot S^z \neq 0:$$

$$S^x = \pm \frac{\sqrt{3}}{3} S, \quad S^y = \pm \frac{\sqrt{3}}{3} S, \quad S^z = \pm \frac{\sqrt{3}}{3} S.$$

i. e. crystallographic directions of the type $[111]$.

In the zero-th approximation we get therefrom the results shown in the table below:

Table I.

Direction	$E_0^{(0)}$	$Q > 0$	$Q < 0$
[100]	$-6NJS^2 + NQS^4$	maximum value of $E_0^{(0)}$	minimum value of $E_0^{(0)}$
[110]	$-6NJS^2 + \frac{1}{2}NQS^4$	intermediate value of $E_0^{(0)}$	intermediate value of $E_0^{(0)}$
[111]	$-6NJS^2 + \frac{1}{3}NQS^4$	minimum value of $E_0^{(0)}$	maximum value of $E_0^{(0)}$

In the first approximation we get the values shown in the table II.

Table II.

Direction	E'_0	$S \neq 1, Q > 0$	$S \neq 1, Q < 0$
[100]	$-6NJS^2 + NQS^4 + 2NQS^2$	maximum value of E'_0	minimum value of E'_0
[110]	$-6NJS^2 + \frac{1}{2}NQS^2(S^2 + 2S + 3)$	intermediate value of E'_0	intermediate value of E'_0
[111]	$-6NJS^2 + \frac{1}{3}NQS^2(S^2 + 4S + 4)$	minimum value of E'_0	maximum value of E'_0

For $S = 1$ the energies for the three main directions are identical.

It can be seen that the direction of easy magnetization depends on the sign of the coefficient of quadrupole interaction Q .

b. For the body centered cubic lattice (e. g. iron, $S = 2$):

$$\vec{R}_h = \frac{a}{2} (\pm \vec{e}_x \pm \vec{e}_y \pm \vec{e}_z), \quad R_h = \frac{a\sqrt{3}}{2},$$

$$\vec{r}_h = \frac{\sqrt{3}}{3} (\pm \vec{e}_x \pm \vec{e}_y \pm \vec{e}_z).$$

There are eight nearest neighbours for each lattice node. In the zero-th approximation ($E_0^{(0)}$) we have:

$$K_0 = -8NJS^2 + 4/9 NQS^4, \quad K_1 = 16/9 NQS^4.$$

In the first approximation we get:

$$K'_0 = -8NJS^2 + 1/9 NQS^2(4S^2 + 16S + 5),$$

$$K'_1 = 16/9 NQS^2 \sigma.$$

In the zero-th approximation we get the values shown in the table III.

Table III.

Direction	$E_0^{(0)}$	$Q > 0$	$Q < 0$
[100]	$-8NJS^2 + \frac{4}{9}NQS^4$	minimum value of $E_0^{(0)}$	maximum value of $E_0^{(0)}$
[110]	$-8NJS^2 + \frac{8}{9}NQS^4$	intermediate value of $E_0^{(0)}$	intermediate value of $E_0^{(0)}$
[111]	$-8NJS^2 + \frac{28}{27}NQS^4$	maximum value of $E_0^{(0)}$	minimum value of $E_0^{(0)}$

The values for the first approximation are shown in the table IV.

Table IV.

Direction	E'_0	$S \neq 1, Q > 0$	$S \neq 1, Q < 0$
[100]	$-8NJS^2 + \frac{1}{3} NQS^2 (4S^2 + 16S + 5)$	minimum value of E'_0	maximum value of E'_0
[110]	$-8NJS^2 + \frac{1}{3} NQS^2 (8S^2 + 8S + 9)$	intermediate value of E'_0	intermediate value of E'_0
[111]	$-8NJS^2 + \frac{1}{27} NQS^2 (28S^2 + 16S + 31)$	maximum value of E'_0	minimum value of E'_0

For $S = 1$ the energies for the above three directions are identical.

The direction of easy magnetization depends on the sign of the coefficient of the quadrupole interaction Q .

c. For the face centered cubic lattice (e. g. nickel, $S \approx 1$):

$$\vec{R}_h = \frac{a}{2} (\pm \vec{e}_x \pm \vec{e}_y), \quad \frac{a}{2} (\pm \vec{e}_x \pm \vec{e}_z), \quad \frac{a}{2} (\pm \vec{e}_y \pm \vec{e}_z),$$

$$R_h = \frac{a\sqrt{2}}{2}, \quad \vec{R}_h = R_h \cdot \vec{r}_h.$$

There are twelve nearest neighbours for each lattice node. In the zero-th approximation we have:

$$K_0 = -12 NJS^2 + NQS^4, \quad K_1 = NQS^4.$$

In the first approximation we get:

$$K'_0 = -12NJS^2 + NQS^2 (S^2 + 2S + 2),$$

$$K'_1 = NQS^2 \sigma.$$

For the zero-th approximation we get the values shown in the table V.

Table V.

Direction	$E_0^{(0)}$	$Q > 0$	$Q < 0$
[100]	$-12NJS^2 + NQS^4$	minimum value of $E_0^{(0)}$	maximum value of $E_0^{(0)}$
[110]	$-12NJS^2 + \frac{5}{4} NQS^4$	intermediate value of $E_0^{(0)}$	intermediate value of $E_0^{(0)}$
[111]	$-12NJS^2 + \frac{4}{3} NQS^4$	maximum value of $E_0^{(0)}$	minimum value of $E_0^{(0)}$

For the first approximation we have the values shown in the table VI.

Table VI.

Direction	E'_0	$S \neq 1, Q > 0$	$S \neq 1, Q < 0$
[100]	$-12NJS^2 + NQS^2(S^2 + 2S + 2)$	minimum value of E'_0	maximum value of E'_0
[110]	$-12NJS^2 + \frac{1}{4}NQS^2(5S^2 + 6S + 9)$	intermediate value of E_0	intermediate value of E'_0
[111]	$-12NJS^2 + \frac{1}{3}NQS^2(4S^2 + 4S + 7)$	maximum value of E'_0	minimum value of E'_0

For $S = 1$ the energies for the above three directions are identical.

The direction of easy magnetization depends on the sign of the coefficient of the quadrupole interaction Q .

The hexagonal lattices:

$$E = a' + b'(S^2)^2 + c'(S^2)^4 - N_\mu \vec{H} \cdot \vec{S}$$

$$= \tilde{K}_0 + \tilde{K}_1 \sin^2 \vartheta + \tilde{K}_2 \sin^4 \vartheta - N_\mu \vec{H} \cdot \vec{S},$$

$$\tilde{K}_0 = a' + b'S^2 + c'S^4, \quad \tilde{K}_1 = -(b' + c'S^2)S^2, \quad \tilde{K}_2 = -c'S^4,$$

ϑ — is the angle between the direction of spontaneous magnetization and the hexagonal axis.

a. For the simple hexagonal lattice:

$$\vec{R}_h = R_h \vec{r}_h = a \vec{r}_h, \quad \vec{r}_h = \pm \vec{e}_x, \pm \vec{e}_x, \pm \frac{1}{2} \vec{e}_x \pm \frac{\sqrt{3}}{2} \vec{e}_y.$$

$\vec{e}_x, \vec{e}_y, \vec{e}_z$ stand for the reciprocally orthogonal unit vectors; \vec{e}_z is the unit vector directed along the hexagonal axis. There are eight nearest neighbours for each lattice node. In the zero-th approximation ($E_0^{(0)}$) we get:

$$\tilde{K}_0 = -8NJS^2 + NPS^2 + NQS^4,$$

$$\tilde{K}_1 = -3/2 NPS^2 - 2NQS^4 < 0.$$

$$\tilde{K}_2 = 17/8 NQS^4 > 0.$$

In the first approximation (E'_0) we have the values:

$$\tilde{K}'_0 = -8NJS^2 + NPS^2 + NQS^2(S^2 + S + 2),$$

$$\tilde{K}'_1 = -3/2 NPS^2 - NQS^2(2S^2 - 3S + 1),$$

$$\tilde{K}'_2 = 17/8 NQS^2 \sigma.$$

If only the six nearest neighbours in the basis plane are taken into account, the easiest magnetization direction is perpendicular to the c -axis.

Moreover, when we take into account also these two neighbours, which are on the c -axis below and above the basis plane, we find that the easiest magnetization direction will still be perpendicular to the hexagonal c -axis, but the minimum of crystal energy for this direction is not as deep as in the former case.

b. For the closely packed hexagonal lattice:

$$\begin{aligned}\vec{R}_h &= R_h \vec{r}_h = a \vec{r}_h, & c &= \sqrt{\frac{8}{3}} a, \\ \vec{r}_h &= \pm \vec{e}_x, \quad \pm \frac{1}{2} \vec{e}_x \pm \frac{\sqrt{3}}{2} \vec{e}_y, \quad \frac{\sqrt{3}}{3} \vec{e}_y \pm \sqrt{\frac{2}{3}} \vec{e}_z, \\ \frac{1}{2} \vec{e}_x - \frac{\sqrt{3}}{6} \vec{e}_y \pm \sqrt{\frac{2}{3}} \vec{e}_z, & -\frac{1}{2} \vec{e}_x - \frac{\sqrt{3}}{6} \vec{e}_y \pm \sqrt{\frac{2}{3}} \vec{e}_z,\end{aligned}$$

There are twelve nearest neighbours for each lattice node. For the zero-th approximation ($E_0^{(0)}$) we get:

$$\begin{aligned}\tilde{K}_0 &= -12NJS^2 + 4/3 NQS^4, \\ \tilde{K}_1 &= -2/3 NQS^4 < 0, \quad \tilde{K}_2 = 7/12 NQS^4 > 0,\end{aligned}$$

For the first approximation (E_0') we have:

$$\begin{aligned}\tilde{K}_0' &= -12NJS^2 + 2/3 NQS^2 (2S^2 + 2S + 5), \\ \tilde{K}_1' &= -2/3 NQS^2 \sigma, \\ \tilde{K}_2' &= 7/12 NQS^2 \sigma.\end{aligned}$$

When we take into account all the twelve nearest neighbours for the closely packed hexagonal lattice, we find, that in comparison with the case of the simple hexagonal lattice the direction of the easiest magnetization leans over toward the hexagonal axis. Whether the easiest magnetization direction lies along the c -axis or deviates from this axis is determined by: S — the spin value, the influence of more distant neighbours and the hexapole interactions.

5. The Influence of Magnetic Field on the Spontaneous Magnetization Direction at 0°K

When no external magnetic field exists, the spontaneous magnetization is directed along one of the easiest magnetization directions. When the external magnetic field \vec{H} forms the angle Θ_0 with the direction of easy magnetization $[h_0 \ k_0 \ l_0]$, the spon-

taneous magnetization will lie in the plane determined by $[h_0 k_0 l_0]$ and \vec{H} , forming an angle Θ with the direction $[h_0 k_0 l_0]$.

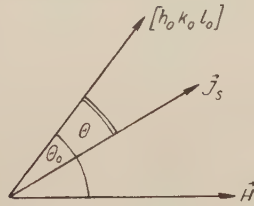


Fig. 1. Directions of easy magnetization, spontaneous magnetization and external magnetic field.

Θ increases with $|\vec{H}|$.

From the condition for minimum of energy E_0 we obtain the dependence of Θ upon the value of \vec{H} :

$$\frac{dE_0}{d\Theta} = 0.$$

$$E_0 = E_{\text{anisotropy}} - H \cdot I_{\text{sat}} \cdot \cos(\Theta_0 - \Theta)$$

we get thus:

$$H = \frac{\frac{dE_{\text{anis.}}}{d\Theta}}{I_{\text{sat.}} \cdot \sin(\Theta_0 - \Theta)}. \quad (21)$$

The magnetization in H direction is:

$$I = I_{\text{sat}} \cdot \cos(\Theta_0 - \Theta). \quad (22)$$

From (21) and (22) we obtain the $I = I(H)$ dependence.

For example, when we take $[h_0 k_0 l_0] = [100]$ and \vec{H} is directed along $[110]$, the direction of spontaneous magnetization in a single crystal of iron will coincide with that of magnetic field when the value of field reaches 345 Oe.

The magnetic field influence on the rotation of spontaneous magnetization was phenomenologically investigated by Bozorth (1936), (1951), Schlechtweg (1936), Tarasov and Bitter (1937).

6. The Dispersion Formulae

The value of E_λ (19) or approximately of U_λ represents the energy of spin wave with wave vector \vec{K}_λ . In the calculations below we consider the nearest neighbours only.

a. For the simple cubic lattice we have:

$$U_{\lambda} = A + a^2 B_x (K_{\lambda}^x)^2 + a^2 B_y (K_{\lambda}^y)^2 + a^2 B_z (K_{\lambda}^z)^2, \quad (23)$$

$$A = a_1 + a_2 \omega + \frac{2\mu}{S} \vec{H} \cdot \vec{S},$$

$$B_x = b + b_1 \alpha_1^2 + b_2 \alpha_1^4,$$

$$B_y = b + b_1 \alpha_2^2 + b_2 \alpha_2^4,$$

$$B_z = b + b_1 \alpha_3^2 + b_2 \alpha_3^4,$$

$$a_1 = 8QS^2 (1 - S),$$

$$a_2 = 8QS\eta,$$

$$\eta = 5S^2 - 7S + 2,$$

$$b = (4J + P) S,$$

$$b_1 = - (3P + 4Q\sigma) S,$$

$$b_2 = 4Q\sigma S.$$

In the present paper the exchange integral J and the pseudodipolar coefficient P have values four times less, the pseudoquadrupolar coefficient Q is sixteen times less and the spin number S two times larger than the corresponding expressions used in the paper of Pal (1955). It follows, that for the magnetic field directed along the spontaneous magnetization, the above mentioned formula is identical with the Pal's formula.

b. For the body centered cubic lattice (e. g. iron $S \approx 2$) we get:

$$U_{\lambda} = A + a^2 B (K_{\lambda})^2 + 2a^2 C (K_{\lambda}^x K_{\lambda}^y) + 2a^2 D (K_{\lambda}^x K_{\lambda}^z) + 2a^2 E (K_{\lambda}^y K_{\lambda}^z), \quad (24)$$

$$A = a_1 + a_2 \omega + \frac{2\mu}{S} \vec{H} \cdot \vec{S},$$

$$B = 4JS - 2/9 QS\sigma + 16/9 QS\omega\sigma,$$

$$C = -4PS \alpha_1 \alpha_2,$$

$$D = -4PS \alpha_1 \alpha_3,$$

$$E = -4PS \alpha_2 \alpha_3,$$

$$a_1 = 64QS (-S^2 + 4/3 S - 1/3),$$

$$a_2 = 64QS\eta.$$

c. For the face centered cubic lattice (e. g. nickel, $S \approx 1$) we obtain:

$$U_{\lambda} = A + a^2 B_x (K_{\lambda}^x)^2 + a^2 B_y (K_{\lambda}^y)^2 + a^2 B_z (K_{\lambda}^z)^2 + 2a^2 C K_{\lambda}^x K_{\lambda}^y + \\ + 2a^2 D K_{\lambda}^x K_{\lambda}^z + 2a^2 E K_{\lambda}^y K_{\lambda}^z, \quad (25)$$

$$A = a_1 + a_2 \omega + \frac{2\mu}{S} \vec{H} \cdot \vec{S},$$

$$B_x = b_0 + b_1 \alpha_1^2 + b_2 \alpha_1^4 + b_3 \omega,$$

$$B_y = b_0 + b_1 \alpha_2^2 + b_2 \alpha_2^4 + b_3 \omega,$$

$$B_z = b_0 + b_1 \alpha_3^2 + b_2 \alpha_3^4 + b_3 \omega,$$

$$C = -(3/2 P + Q\sigma) S \alpha_1 \alpha_2,$$

$$D = -(3/2 P + Q\sigma) S \alpha_1 \alpha_3,$$

$$E = -(3/2 P + Q\sigma) S \alpha_2 \alpha_3,$$

$$a_1 = 4QS(S^2 + 17S + 2),$$

$$a_2 = -4QS\eta,$$

$$b_0 = 1/4 (16JS + PS - 2QS\sigma),$$

$$b_1 = -1/4 (3PS + 4QS\sigma),$$

$$b_2 = -1/2 QS\sigma,$$

$$b_3 = QS\sigma.$$

d. For the simple hexagonal lattice we have:

$$U_{\lambda} = A + a^2 B (K_{\lambda}^x)^2 + a^2 C (K_{\lambda}^y)^2 + a^2 D (K_{\lambda}^z)^2 + 2a^2 E K_{\lambda}^x K_{\lambda}^y, \quad (26)$$

$$A = a_1 + a_2 \alpha_3^2 + a_3 \alpha_3^4 + \frac{2\mu}{S} \vec{H} \cdot \vec{S},$$

$$B = b_1 + b_2 \alpha_3^2 + b_3 \alpha_3^4 + b_4 \alpha_1^2 + b_5 \alpha_1^4,$$

$$C = c_1 + c_2 \alpha_3^2 + c_3 \alpha_3^4 + c_4 \alpha_1^2 + c_5 \alpha_1^4,$$

$$D = d_1 + d_2 \alpha_3^2 + d_3 \alpha_3^4,$$

$$E = e_1 + e_2 \alpha_1^2 + e_3 \alpha_2^2,$$

$$a_1 = 3PS + 1/2 QS(-9S^2 - S + 6),$$

$$a_2 = -9PS + QS(39S^2 - 47S + 14),$$

$$a_3 = 1/2 QS(-85S^2 + 119S - 34),$$

$$b_1 = 6JS + 3/8 PS - 3/8 QS\sigma,$$

$$b_2 = 9/8 PS - 3/4 QS\sigma,$$

$$b_3 = 9/8 QS\sigma,$$

$$b_4 = -9/4 PS - 3QS\sigma,$$

$$\begin{aligned}
b_5 &= 3QS\sigma, \\
c_1 &= 6JS - 15/8 PS - 9/8 QS\sigma, \\
c_2 &= 27/8 PS - 3/4 QS\sigma, \\
c_3 &= 27/8 QS\sigma, \\
c_4 &= 9/4 PS + 3QS\sigma, \\
c_5 &= -3QS\sigma, \\
d_1 &= 4JS + PS, \\
d_2 &= -3PS - 4QS\sigma, \\
d_3 &= 4QS\sigma, \\
e_1 &= -1/2 (9P + 6Q\sigma) S \alpha_1 \alpha_2, \\
e_2 &= 3/2 QS\sigma \alpha_1 \alpha_2, \\
e_3 &= 9/2 Q\sigma S \alpha_1 \alpha_2.
\end{aligned}$$

For the case of axial symmetry we get:

$$U_\lambda = A + a^2 B (K_\lambda^x)^2 + a^2 C (K_\lambda^y)^2 + a^2 D (K_\lambda^z)^2, \quad (27)$$

$$A = a_1 + a_2 \alpha_3^2 + a_3 \alpha_3^4 + \frac{2\mu}{S} \vec{H} \cdot \vec{S},$$

$$B = b_1 + b_2 \alpha_3^2 + b_3 \alpha_3^4,$$

$$C = c_1 + c_2 \alpha_3^2 + c_3 \alpha_3^4,$$

$$D = d_1 + d_2 \alpha_3^2 + d_3 \alpha_3^4,$$

where a_1, a_2, a_3 have the values as above.

$$b_1 = 6JS - 15/8 PS - 3/8 QS\sigma,$$

$$b_2 = 27/8 PS - 15/4 QS\sigma,$$

$$b_3 = 33/8 QS\sigma,$$

$$c_1 = 6JS + 3/8 PS - 9/8 QS\sigma,$$

$$c_2 = 9/8 PS + 3/4 QS\sigma,$$

$$c_3 = 3/8 QS\sigma,$$

$$d_1 = 4JS + PS,$$

$$d_2 = -3PS - 4QS\sigma,$$

$$d_3 = 4QS\sigma.$$

This formula is identical with that of Pal (1955) by data as shown above in the discussion of the formula (23).

e. For the closely packed hexagonal lattice we get:

$$U_{\lambda} = A + a^2 B (K_{\lambda}^x)^2 + a^2 C (K_{\lambda}^y)^2 + a^2 D (K_{\lambda}^z)^2 + 2a^2 E K_{\lambda}^x K_{\lambda}^y + \\ + 2a^2 F K_{\lambda}^x K_{\lambda}^z + 2a^2 G K_{\lambda}^y K_{\lambda}^z, \quad (28)$$

$$A = a_1 + a_2 \alpha_3^2 + a_3 \alpha_3^4 + \frac{2\mu}{S} \vec{H} \cdot \vec{S},$$

$$B = b_1 + b_2 \alpha_3^2 + b_3 \alpha_3^4 + b_4 \alpha_1^2 + b_5 \alpha_1^4 + b_6 \alpha_1^2 \alpha_3^2,$$

$$C = c_1 + c_2 \alpha_3^2 + c_3 \alpha_3^4 + c_4 \alpha_2^2 + c_5 \alpha_2^4 + c_6 \alpha_2^2 \alpha_3^2,$$

$$D = d_1 + d_2 \alpha_3^2 + d_3 \alpha_3^4 + d_4 \alpha_1^2 + d_5 \alpha_1^4 + d_6 \alpha_1^2 \alpha_3^2,$$

$$E = e_1 + e_2 \alpha_2^2 + e_3 \alpha_3^2,$$

$$F = f_1 + f_2 \alpha_2^2 + f_3 \alpha_3^2,$$

$$G = g_1 + g_2 \alpha_2^2 + g_3 \alpha_3^2,$$

$$a_1 = -QS(S^2 + 5S - 6),$$

$$a_2 = -2QS\eta,$$

$$a_3 = 5/3QS\eta,$$

$$b_1 = -8JS - 3/2 PS - (8 + 7/12) QS\sigma,$$

$$b_2 = -1/2 PS + 58/3 QS\sigma,$$

$$b_3 = -(10 + 5/9) QS\sigma,$$

$$b_4 = 5PS + 64/3 QS\sigma,$$

$$b_5 = -12 QS\sigma,$$

$$b_6 = -(19 + 1/6) QS\sigma,$$

$$c_1 = -8JS - 15/2 PS + 1/4 QS\sigma,$$

$$c_2 = -1/2 PS + 5/6 QS\sigma,$$

$$c_3 = -23/36 QS\sigma,$$

$$c_4 = 5PS - 3/2 QS\sigma,$$

$$c_5 = -73/18 QS\sigma,$$

$$c_6 = 9/2 QS\sigma,$$

$$d_1 = -8JS - 6PS + 19/27 QS\sigma,$$

$$d_2 = -6PS - 2/27 QS\sigma,$$

$$d_3 = 31/27 QS\sigma,$$

$$d_4 = 8/27 QS\sigma,$$

$$d_5 = 0,$$

$$\begin{aligned}
d_6 &= -8/27 \, Q S \sigma, \\
e_1 &= 1/2 \, (P + 1/3 \, Q \sigma) \, S \alpha_1 \alpha_2, \\
e_2 &= 1/9 \, Q \sigma \, S \alpha_2 \alpha_2, \\
e_3 &= -7/6 \, Q \sigma \, S \alpha_1 \alpha_2, \\
f_1 &= (4P + 7/3 \, Q \sigma) \, S \alpha_1 \alpha_3, \\
f_2 &= -2/3 \, Q \sigma \, S \alpha_1 \alpha_3, \\
f_3 &= -29/9 \, Q \sigma \, S \alpha_1 \alpha_3, \\
g_1 &= 4/3 \, (P + Q \sigma) \, S \alpha_2 \alpha_3, \\
g_2 &= 32/27 \, Q \sigma \, S \alpha_2 \alpha_3, \\
g_3 &= 4/27 \, Q \sigma \, S \alpha_2 \alpha_3.
\end{aligned}$$

For the case of axial symmetry we obtain:

$$U_\lambda = A + a^2 B (K_\lambda^x)^2 + a^2 C (K_\lambda^y)^2 + a^2 D (K_\lambda^z)^2 + 2a^2 F K_\lambda^x K_\lambda^z, \quad (29)$$

$$A = a_1 + a_2 \alpha_3^2 + a_3 \alpha_3^4 + \frac{2\mu}{S} \vec{H} \cdot \vec{S}.$$

$$B = b_1 + b_2 \alpha_3^2 + b_3 \alpha_3^4,$$

$$C = c_1 + c_2 \alpha_3^2 + c_3 \alpha_3^4,$$

$$D = d_1 + d_2 \alpha_3^2 + d_3 \alpha_3^4,$$

$$F = f_1 + f_2 \alpha_3^2,$$

$$a_1 = -QS(S^2 + 5S - 6),$$

$$a_2 = -2QS\eta,$$

$$a_3 = 5/3 \, QS\eta,$$

$$b_1 = -8JS + 7/2 \, PS + 3/4 \, QS\sigma,$$

$$b_2 = -11/2 \, PS + 22 \, QS\sigma,$$

$$b_3 = -(3 + 7/18) \, QS\sigma,$$

$$c_1 = -8JS - 15/2 \, PS + 1/4 \, QS\sigma,$$

$$c_2 = -1/2 \, PS + 5/6 \, QS\sigma,$$

$$c_3 = -23/36 \, QS\sigma,$$

$$d_1 = -8JS - 15/2 \, PS + 1/4 \, QS\sigma,$$

$$d_2 = -6PS - 10/27 \, QS\sigma,$$

$$d_3 = 39/27 \, QS\sigma,$$

$$f_1 = (4P + 7/3 \, Q\sigma) \, S \alpha_1 \alpha_3,$$

$$f_2 = -29/9 \, Q\sigma \, S \alpha_1 \alpha_3.$$

Coefficients of K_λ^x , K_λ^y , K_λ^z consist each of an isotropic and an anisotropic part. The anisotropic part, which is of magnetic pseudodipole and pseudoquadrupole origin, amounts to about two percent of the isotropic one.

7. Free Energy

Free energy of crystal is given by formula (Appendix II):

$$F = E_0 + kT \sum_{\lambda} \ln \left[1 - \exp \left(-\frac{U_{\lambda}}{kT} \right) \right], \quad (30)$$

Going over from the sum to the integral (Appendix III) we get

$$\begin{aligned} F = E_0 + kT \frac{N}{N_1 (2\pi)^3} \int_{-\infty}^{+\infty} \ln \left\{ 1 - \exp \left[\left(-\frac{1}{kT} \right) (A + a^2 B_x (K_\lambda^x)^2 + \right. \right. \\ \left. \left. + a^2 B_y (K_\lambda^y)^2 + a^2 B_z (K_\lambda^z)^2 + 2a^2 CK_\lambda^x K_\lambda^y + 2a^2 DK_\lambda^x K_\lambda^z + \right. \right. \\ \left. \left. 2a^2 EK_\lambda^y K_\lambda^z) \right] \right\} dK_\lambda^x \cdot dK_\lambda^y \cdot dK_\lambda^z, \end{aligned} \quad (31)$$

where N_1 is the number of lattice sites in one simple cell. We transform the above quadratic form into the canonic one.

$$\begin{aligned} a^2 [B_x (K_\lambda^x)^2 + B_y (K_\lambda^y)^2 + B_z (K_\lambda^z)^2 + 2CK_\lambda^x K_\lambda^y + 2DK_\lambda^x K_\lambda^z + 2EK_\lambda^y K_\lambda^z] \\ = a^2 [\chi_1 (K_\lambda^x)^2 + \chi_2 (K_\lambda^y)^2 + \chi_3 (K_\lambda^z)^2], \end{aligned} \quad (32)$$

where χ_1 , χ_2 and χ_3 are the real roots of equation:

$$\begin{vmatrix} B_x - \chi & C & D \\ C & B_y - \chi & E \\ D & E & B_z - \chi \end{vmatrix} = 0,$$

The coefficients of the transformation, which leads to the canonic form of (32) are given by the following equations:

$$\begin{pmatrix} B_x - \chi_{1\kappa} & C & D \\ C & B_y - \chi_{2\kappa} & E \\ D & E & B_z - \chi_{3\kappa} \end{pmatrix} \begin{pmatrix} \beta_{1\kappa} \\ \beta_{2\kappa} \\ \beta_{3\kappa} \end{pmatrix} = 0,$$

thus

$$\begin{pmatrix} K_\lambda^{x'} \\ K_\lambda^{y'} \\ K_\lambda^{z'} \end{pmatrix} = \begin{pmatrix} \beta_{11} & \beta_{21} & \beta_{31} \\ \beta_{12} & \beta_{22} & \beta_{32} \\ \beta_{13} & \beta_{23} & \beta_{33} \end{pmatrix} \begin{pmatrix} K_\lambda^x \\ K_\lambda^y \\ K_\lambda^z \end{pmatrix} = \beta \begin{pmatrix} K_\lambda^x \\ K_\lambda^y \\ K_\lambda^z \end{pmatrix}$$

The inverse transformation will have the following form:

$$\begin{pmatrix} K_{\lambda}^x \\ K_{\lambda}^y \\ K_{\lambda}^z \end{pmatrix} = \begin{pmatrix} \beta_{11} & \beta_{12} & \beta_{13} \\ \beta_{21} & \beta_{22} & \beta_{23} \\ \beta_{31} & \beta_{32} & \beta_{33} \end{pmatrix} \begin{pmatrix} K_{\lambda}^{x'} \\ K_{\lambda}^{y'} \\ K_{\lambda}^{z'} \end{pmatrix},$$

When we substitute:

$$a \sqrt{\frac{\chi_1}{kT}} \cdot K_{\lambda}^{x'} = u, \quad a \sqrt{\frac{\chi_2}{kT}} \cdot K_{\lambda}^{y'} = v, \quad a \sqrt{\frac{\chi_3}{kT}} \cdot K_{\lambda}^{z'} = \omega,$$

we get

$$F = E_0 + (kT)^{\frac{5}{2}} \cdot \frac{N\beta}{N_1 (2\pi)^2 \cdot a^3 \sqrt{\chi_1 \chi_2 \chi_3}} \cdot L(\psi), \quad (33)$$

where

$$L(\psi) = \int_{-\infty}^{+\infty} \ln \{1 - \exp[-\psi - (u^2 + v^2 + \omega^2)]\} du \cdot dv \cdot d\omega, \text{ with } \psi = \frac{A}{kT}.$$

Introducing spherical coordinates ϱ , ξ , ζ and putting $\varrho^2 = t$ we get:

$$L(\psi) = 2\pi \int_0^{\infty} \ln [1 - \exp(-\psi - t)] \sqrt{t} \cdot dt.$$

Performing the integration (Appendix IV) we get:

$$L(\psi) = -\Gamma\left(\frac{3}{2}\right) \sum_{n=1}^{\infty} \frac{\exp(-n\psi)}{n^{5/2}} = -\Gamma\left(\frac{3}{2}\right) \cdot \Lambda(\psi), \quad (34)$$

We calculate approximatively the $\Lambda(\psi)$ sum using Euler's method (Bieberbach 1930, Valenta 1955):

$$\begin{aligned} \Lambda(\psi) &= \sum_{n=1}^{\infty} \frac{\exp(-n\psi)}{n^{5/2}} = \sum_{n=1}^{\infty} g(n) = \int_1^{\infty} g(x) dx + \frac{1}{2} [g(\infty) + g(1)] + \\ &+ \frac{\tilde{B}_1}{2} [g'(\infty) - g'(1)] + \int_1^{\infty} g'''(x) \cdot W(x) \cdot dx, \end{aligned}$$

where

$$g(x) = x^{-\frac{5}{2}} \cdot \exp(-\psi x), \quad \tilde{B}_1 = \frac{1}{6}, \quad W(x) = \sum_{n=1}^{\infty} \frac{\sin 2\pi n x}{4\pi^3 n^3}.$$

After some calculations we obtain:

$$A(\psi) = (11/8 - 5/4 \psi) \exp(-\psi) + 4/3 \psi \sqrt{\pi\psi} \cdot [1 - \Phi(\sqrt{\psi})] + R(\psi),$$

where

$$\Phi(\sqrt{\psi}) = \frac{2}{\sqrt{\pi}} \cdot \int_0^{\sqrt{\psi}} \exp(-\mu^2) d\mu,$$

is the Gauss integral (Jahnke, Emde 1938).

We proceed now to the estimate of $R(\psi)$:

$$\begin{aligned} |R(\psi)| &\leq \int_1^\infty |g'''(x)| \cdot |W(x)| dx \leq \frac{1}{4\pi^3} \sum_{n=1}^\infty \frac{1}{n^3} \int_1^\infty |g'''(x)| dx < 10^{-2} \int_1^\infty |g'''(x)| dx \\ &= 10^{-2} (\psi^3 \cdot I_{-5/2} + 3 \cdot 5/2 \cdot \psi^2 \cdot I_{-7/2} + 3 \cdot 5/2 \cdot 7/2 \cdot \psi \cdot I_{-9/2} + 5/2 \cdot 7/2 \cdot 9/2 \cdot I_{-11/2}) \\ &= 10^{-2} (\psi^2 + 5\psi + 35/4) \exp(-\psi), \end{aligned}$$

where

$$I_{-\frac{m}{2}} = \int_1^\infty \exp(-\psi x) x^{-\frac{m}{2}} dx, \quad I_{-\frac{m}{2}} = \frac{2}{m-2} \left[\exp(-\psi) - \psi \cdot I_{-\frac{m-2}{2}} \right].$$

For $\psi \leq 0.1$ the rest $R(\psi)$ represents maximum 6.5 percent of $A(\psi)$ value.

Using the formula (33) we shall now calculate as an example the free energy of simple cubic lattice (for $\psi \leq 0.1$):

$$\begin{aligned} F &= \tilde{A} + \tilde{B} (kT)^{5/2} + \tilde{C} (kT)^{3/2} + \tilde{D} (kT)^{1/2} + \\ &+ [\tilde{E} (kT)^{3/2} + \tilde{G} (kT)^{1/2} + \tilde{L}] H \cdot \cos(\vec{S}, \vec{H}) + K_1 \omega, \\ K_1 &= \tilde{\alpha} + \tilde{\beta} (kT)^{5/2} + \tilde{\gamma} (kT)^{3/2} + \tilde{\delta} (kT)^{1/2} + \\ &+ [\tilde{\varepsilon} (kT)^{3/2} + \tilde{k} (kT)^{1/2}] H \cos(\vec{S}, \vec{H}), \\ \tilde{A} &= -6NJS^2 + NQS^2(S^2 + 2), \\ \tilde{B} &= 11/8 \Delta \cdot \varepsilon, \\ \tilde{C} &= \Delta \cdot \varepsilon \cdot \gamma \cdot a_1, \\ \tilde{D} &= \Delta \cdot \varepsilon \cdot \Xi \cdot a_1^2, \\ \tilde{E} &= 2\mu \cdot \Delta \cdot \varepsilon \cdot \gamma, \\ \tilde{G} &= 2\mu \cdot a_1 \cdot \Delta \cdot \varepsilon \cdot \Xi, \end{aligned}$$

$$\begin{aligned}
\tilde{L} &= -N\mu S, \\
\tilde{\alpha} &= -2NQ S\sigma, \\
\tilde{\beta} &= 11/8 \Delta \cdot \zeta, \\
\tilde{\gamma} &= \Delta \cdot \gamma \cdot \zeta \cdot a_1, \\
\tilde{\delta} &= 2\Delta \cdot \varepsilon \cdot \Xi \cdot a_1 \cdot a_2, \\
\tilde{\varepsilon} &= 2\mu \cdot \Delta \cdot \gamma \cdot \zeta, \\
\tilde{k} &= 2\mu \cdot \Delta \cdot \zeta \cdot \Xi \cdot a_1, \\
\Delta &= -\frac{N \cdot \Gamma(\frac{3}{2})}{(2\pi)^2 a^3}, \\
\varepsilon &= (4JS)^{-3/2} \cdot \left(1 + \frac{3P}{8J}\right), \\
\Xi &= 5/3 \sqrt{\pi} [1 - \Phi(\sqrt{\psi})] + 31/16, \\
\gamma &= 1/24 \{4 \sqrt{\pi} [1 - \Phi(\sqrt{\psi})] - 63\}, \\
\zeta &= 1/4 (4JS)^{-7/2} \cdot S^2 (9P^2 + 64JQ\eta).
\end{aligned}$$

Appendix I

Let us introduce two orthogonal systems of axes:

1. a system x, y, z which is rigidly bound with the crystallographical structure of lattice;

2. a system x', y', z' whose z' -axis is directed along the direction of spontaneous magnetization.

We can express the spin operators in \hat{S}_i representation in $\hbar/2$ units by Bose operators \hat{b}_i, \hat{b}_i^* ,

$$\begin{aligned}
\hat{S}_i^x &= \sqrt{S_i} \cdot [f(\hat{n}_i) \hat{b}_i + \hat{b}_i^* f(\hat{n}_i)], \\
\hat{S}_i^y &= \frac{\sqrt{S_i}}{i} [f(\hat{n}_i) \hat{b}_i - \hat{b}_i^* f(\hat{n}_i)], \\
\hat{S}_i^z &= S_i - 2\hat{b}_i^* \hat{b}_i.
\end{aligned} \tag{35}$$

The transformations (35) are known from the paper of Holstein and Primakoff (1940).

The $\hat{S}^x, \hat{S}^y, \hat{S}^z$ operators are matrices, which transform as simple polar vectors.

The spin operators in the system of coordinates x, y, z are:

$$\begin{aligned}
\hat{S}^x &= \cos(x, x') \hat{S}^{x'} + \cos(x, y') \hat{S}^{y'} + \cos(x, z') \hat{S}^{z'}, \\
\hat{S}^y &= \cos(y, x') \hat{S}^{x'} + \cos(y, y') \hat{S}^{y'} + \cos(y, z') \hat{S}^{z'}, \\
\hat{S}^z &= \cos(z, x') \hat{S}^{x'} + \cos(z, y') \hat{S}^{y'} + \cos(z, z') \hat{S}^{z'}.
\end{aligned} \tag{36}$$

When the y' -axis lies in the xy plane, i. e. when $\angle(z, y') = \pi/2$ (see Fig. 2), we obtain for \hat{S}^x , \hat{S}^y , and \hat{S}^z the formula (3).

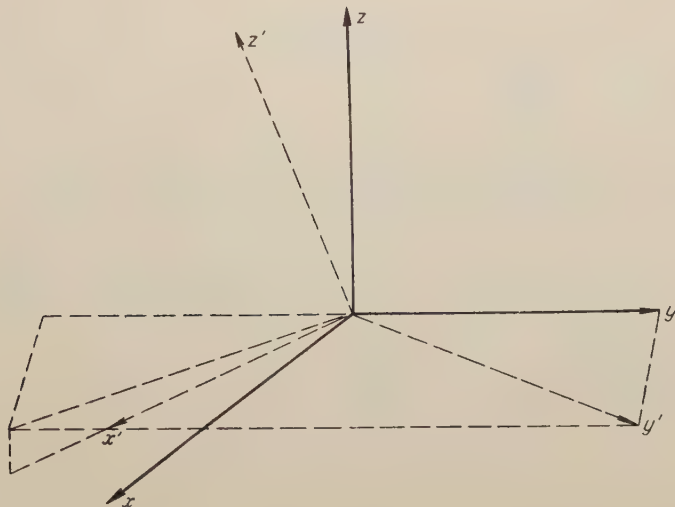


Fig. 2.

In the \hbar units these formulae take the form:

$$\hat{S}_I^{\alpha} = S_I^{\alpha} \left(1 - \frac{\hat{n}_I}{S_I} \right) + \frac{1}{2} \Omega_I^{\alpha} f(\hat{n}_I) \hat{b}_I + \frac{1}{2} \Omega_I^{\alpha*} \hat{b}_I^* f(\hat{n}_I),$$

When S_I^z tends to S_I , $S_I^y = 0$ and S_I^x tends to zero, or when $\angle(y, y') = 0$, $\angle(x, x') \rightarrow 0$ and $\angle(z, z') \rightarrow 0$ we get transformation formulae of Holstein and Primakoff.

$$\hat{S}_I^x = \frac{\sqrt{2S_I}}{2} [f(\hat{n}_I) \hat{b}_I + \hat{b}_I^* \cdot f(\hat{n}_I)],$$

$$\hat{S}_I^y = \frac{\sqrt{2S_I}}{2i} [f(\hat{n}_I) \hat{b}_I - \hat{b}_I^* \cdot f(\hat{n}_I)],$$

$$\hat{S}_I^z = S_I - \hat{b}_I^* \cdot \hat{b}_I, \quad f(\hat{n}_I) = \sqrt{1 - \frac{\hat{n}_I}{S_I}}.$$

Tiablikov (1956a a. b) has also obtained the transformation (3) using a method of approximate second quantization.

It can be seen that the transformation formulae of Holstein — Primakoff and Tiablikov are the special cases of (36) formulae.

Appendix II

Free energy is given by:

$$F = -kT \ln Z$$

where Z is the sum of states.

$$\begin{aligned} Z &= \sum_{\{n_\lambda\}=0}^{\infty} \exp \left[-\frac{1}{kT} \left(E_0 + \Delta E + \sum_{\lambda} E_{\lambda} n_{\lambda} \right) \right] \\ &= \exp \left[-\frac{1}{kT} (E_0 + \Delta E) \right] \prod_{\lambda} \left[\sum_{n_{\lambda}=0}^{\infty} \exp \left(-\frac{1}{kT} E_{\lambda} n_{\lambda} \right) \right] \\ &\cong \exp \left[-\frac{1}{kT} (E_0 + \Delta E) \right] \prod_{\lambda=-\infty}^{\infty} \frac{1}{1 - \exp \left(-\frac{1}{kT} E_{\lambda} \right)}, \\ F &= E_0 + \Delta E + kT \sum_{\lambda=-\infty}^{+\infty} \ln \left[1 - \exp \left(-\frac{E_{\lambda}}{kT} \right) \right]. \end{aligned}$$

Appendix III

We can replace the summations $\sum_{(\lambda_1, \lambda_2, \lambda_3)}$ which extend from $-\frac{1}{2} G_i$ to $\frac{1}{2} G_i - 1$ by summations from $-\infty$ to $+\infty$, because the short spin waves induce only negligible corrections to the value of free energy. The function which is summed, depends on the scalar products, which are invariants for transformation to another coordinates system.

Instead of summing over the indices $\lambda_1, \lambda_2, \lambda_3$, which describe any translation lattice with cubic or hexagonal arrangement, we shall sum over $\lambda_x, \lambda_y, \lambda_z$, which correspond to a simple cubic lattice. In regard of the very high values of G_x, G_y, G_z , the summations over $\lambda_x, \lambda_y, \lambda_z$ can be replaced by integrations:

$$\sum_{\lambda} f(\vec{K}_{\lambda}) = \frac{G_x G_y G_z}{(2\pi)^3} \cdot \int f(\vec{K}) d\vec{K}.$$

We calculate G_x, G_y, G_z from the following condition:

$$\sum_{\lambda} 1 \rightarrow \frac{G_x G_y G_z}{(2\pi)^3} \int d\vec{K},$$

where the integration is extended over the first Brillouin zone. For cubic lattices

$G_x G_y G_z$ gives the number of simple cubic cells $= N/N_1$. N stands for the overall number of lattice sites, and N_1 for the number of sites lattice in one simple cubic cell.

For hexagonal lattices there is a fractional value of N_1 .

Appendix IV

To calculate the integral:

$$L'(\psi) = \int_0^{\infty} \frac{t^{1/2}}{\exp(\psi + t) - 1} dt.$$

we consider the more general integral:

$$\begin{aligned} \int_0^{\infty} \frac{t^{p-1}}{\exp(\psi + t) - 1} dt &= \int_0^{\infty} t^{p-1} \left\{ \sum_{n=1}^{\infty} \exp[-n(\psi + t)] \right\} dt \\ &= \sum_{n=1}^{\infty} \int_0^{\infty} t^{p-1} \exp(-n\psi) \exp(-nt) dt, \end{aligned}$$

Putting $nt = q$ we get therefrom

$$\sum_{n=1}^{\infty} \frac{\exp(-n\psi)}{n^p} \int_0^{\infty} q^{p-1} \exp(-q) dq = \Gamma(p) \sum_{n=1}^{\infty} \frac{\exp(-n\psi)}{n^p};$$

Hence

$$L'(\psi) = \Gamma\left(\frac{3}{2}\right) \sum_{n=1}^{\infty} \frac{\exp(-n\psi)}{n^{3/2}},$$

$$L(\psi) = -\Gamma\left(\frac{3}{2}\right) \sum_{n=1}^{\infty} \frac{\exp(-n\psi)}{n^{5/2}}.$$

This is the (34) formula.

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ELECTRICAL RELAXATION IN NI—ZN FERRITE

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The electric and magnetic properties of iron deficient Ni-Zn ferrite were investigated to obtain an explanation of the mechanism of dielectric relaxation. The relaxation observed was found to be related to electron diffusion, and not to inhomogeneous structure.

Introduction

The electric properties of ferrites are as yet insufficiently well known, notwithstanding the fact that these are materials of great importance for basic investigations and practical application. Their unusually high dielectric constant and its dispersion are of especial interest. A number of papers (Polder 1950, Koops 1951, Fairweather & Frost 1953, Volger 1954, Yoffe et al. 1957, Peters & Standley 1958) deal with these properties. The first four give an explanation of the dielectric properties of ferrites based on the inhomogeneous structure of polycrystalline ceramics. Koops attempted to explain the dielectric properties of Ni—Zn ferrite by assuming the presence of two layers within the grains of the polycrystalline material. The equivalent RC system yielded frequency dependent resultant capacity, losses and resistance in accordance with the curves of these quantities as obtained by measurement. The theory was generalized recently (Parker & Smith, 1958). It would seem, however, that agreement with the theoretically predicted results has been due more to the choice of definitions (Hippel 1954, p. 88), whereas in reality the phenomena observed were caused by relaxation effects detected at about the same time and related to electron diffusion (Kaniichi-Kamiyoshi 1951). This is suggested by some doubts as to whether the assumptions on which Koops has based his computations are justified. According to his theory very thin boundary layers*) would have to surround grain cores of greater conductivity. However, it is well-known that the rise in conductivity of ferrites is related to the appearance of Fe^{++} ions (Wijn 1953, Domenicali 1950, Calhoun 1954) as a result of

* Some authors place the thickness of the boundary layer at about 1 Å (Volger 1954).

partial reduction in the process of heating which should be greatest at the surface of the grains. It would seem that re-oxidation during cooling should be impeded by the fact that the Fe^{++} ions are chemically bound. If such is the case in reality, additional difficulties arise for Koops theory, on account of his assumption, that the dielectric constant of the boundary layers has the same value as that of the grain cores. This assumption is contradicted by results cited by the same author and showing that both the conductivity and dielectric constant depend strongly on the Fe^{++} ions contents. In this context it is interesting to mention also results by Yoffe, Khvostyenko and Zonn, who proved i. a. that, in CO—Zn ferrite, the properties of polycrystalline ceramics resemble those of monocrystals. Finally, Peters and Standley carried out measurements of the dielectric properties of Mg—Mn ferrites that did not corroborate Koops' results.

The present investigation is the first of a series aimed at explaining the mechanism of dielectric relaxation in ferrites.

Results

$\text{ZnO}_{0.7}$ $\text{NiO}_{0.5}$ $\text{Fe}_2\text{O}_{30.3}$ samples.

The samples were prepared using standard techniques, by heating a compressed mixture of oxides at 1200°C and letting it cool gradually with access of air. The grain size was about 1μ . X-ray analysis, carried out by Mr Przedmojski of the Chair of General Physics B of the Warsaw Polytechnical School, showed the samples to contain ZnO in addition to material of spinel structure. The lattice constant amounted to 8.40 \AA . The method of preparation was found to influence the properties critically. The dielectric and magnetic properties were measured by the resonance method using an especially adapted Ferisol French-made Q-meter. A general diagram of the measuring device is given in Fig. 1. The dielectric measurements were carried out with the condenser C_x especially adapted to use throughout the range of -60° to $+300^\circ\text{C}$.

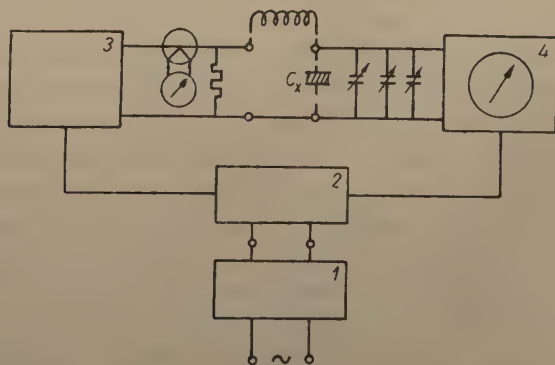


Fig. 1. Simplified diagram of the measuring device 1. — Magnetic stabilizer, 2. — Power supply, 3. — 50 kc — 70 Mc oscillator, 4. — Vacuum-tube voltmeter.

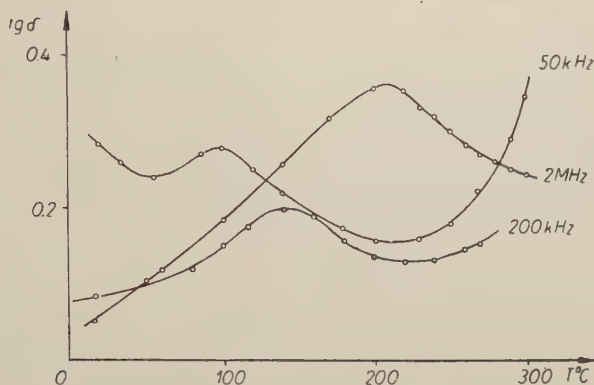


Fig. 2. Temperature dependence of dielectric losses at different frequencies.

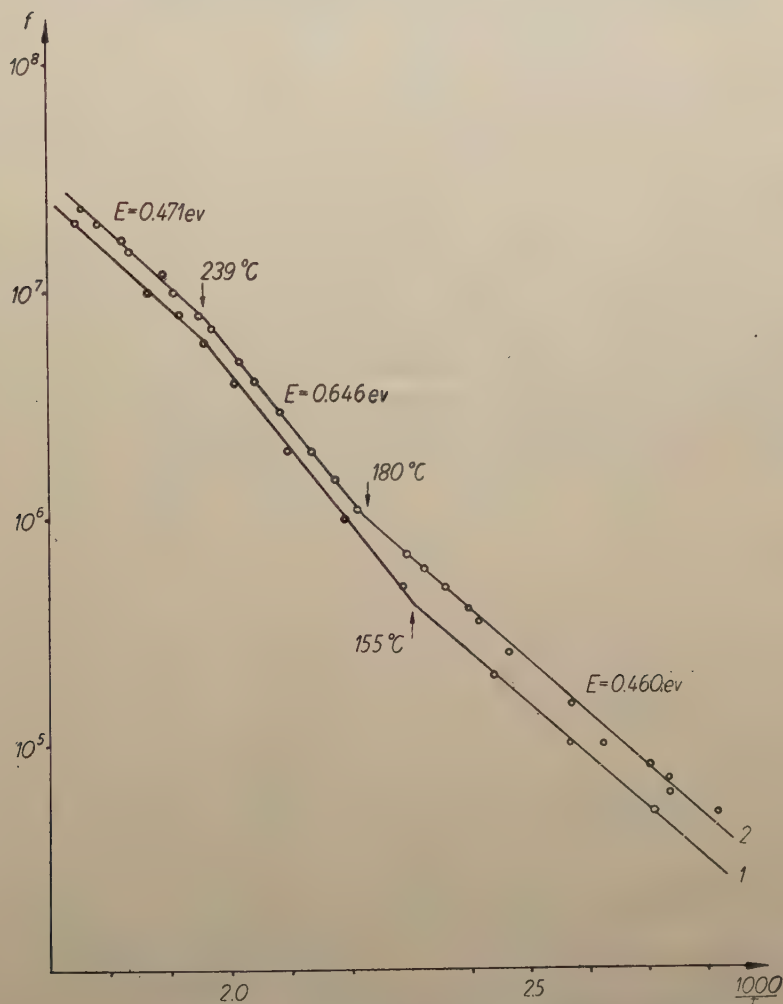


Fig. 3. Temperature of maximum of the dielectric losses vs frequency.

Coating with electrodes of any kind (graphite, silver) was found to present no advantages in the case considered. Checking by dielectric measurements and by measuring the conductivity (using a Wheatstone bridge of high precision) proved that heating the sample to about 300°C produces considerable changes in its properties after some time. This could be avoided by using plate electrodes pressed onto the sample. Although in the latter case considerable difficulties arise if the exact absolute values of the conductivity, dielectric constant and losses are to be measured, carrying out the measurements with all possible precautions and care yields the thermal dependence of the foregoing properties with good reproducibility, which is especially important. Moreover, plate electrodes held pressed to the sample reduce total losses by lowering the contribution from conduction, thus enhancing the degree of precision of the dielectric measurements. Measurements were made for different temperatures at constant values of the frequency. The permeability was measured on a toroidal sample with a single copper winding. In this case, the dielectric losses were neglected. An ultrathermostat was used for investigating both the electric and magnetic properties; however, the samples did not contact the silicone oil used in thermostat, as it was found that even traces of oil in the sample bring about considerable changes in its properties.

Typical curves of the losses are shown in Fig. 2, wherein characteristic maxima, shifting towards higher temperatures as the measuring field frequency rises, are seen. From a number of such curves, Fig. 3 was obtained, showing the relation between the frequency and the temperature at which maximum losses occur. Curve 2 was obtained with a sample additionally heated at 360°C during 5 hours. The anomaly about 240°C is related to the Curie point, as proved by measurements of the initial permeability. The results are shown in Fig. 4. Maximum magnetic losses occur at the temperature at which the permeability drops to 0.8 of its maximum value. Measurements at

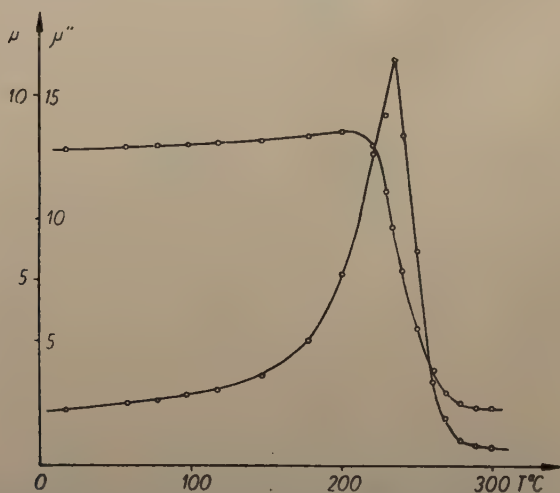


Fig. 4. Temperature dependence of the initial permeability at 10 Mc.

other frequencies yield identical results. For comparison, the measurements of the electric conductivity shown in Fig. 5 were carried out. The latter reveal a discontinuity at 155°C. At the Curie temperature there is no such discontinuity. Curve 2 was obtained after the sample had been heated at 360°C for 5 hours. The discontinuity is displaced towards higher temperatures. Curve 3 shows measurements on a sample that had been additionally polished down to about 50% of its original thickness.

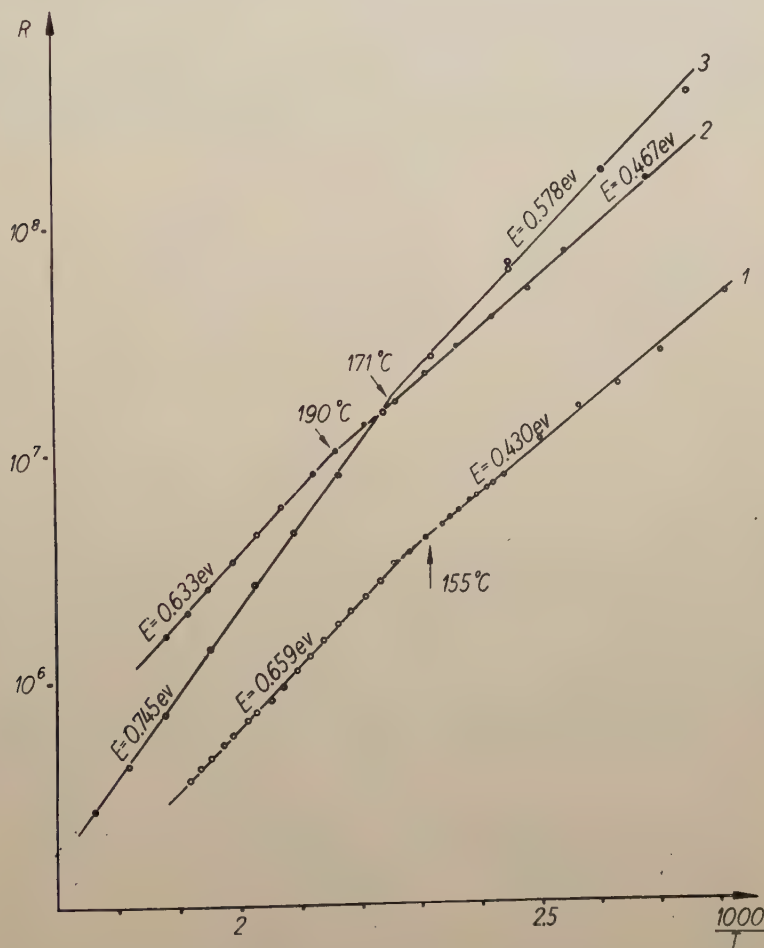


Fig. 5. Temperature dependency of the electric conductivity.

This proves that if the results are to be reproducible, uncontrolled polishing cannot be employed. A rise in the activation energy shows the deficit in oxygen to be related to the sample surface.

A measurement of the thermoelectric power proved the ferrite to possess electron conductivity.

Discussion

The foregoing results cannot be explained by Koops' theory. Although it is difficult to give a correct interpretation in the case under consideration, it can be shown that even in so complicated a case important information may be deduced.

In principle, the dielectric relaxation observed in polycrystalline ferrites might be interpreted as arising from inhomogeneous structure (Wagner, 1914). Eq. (40) of the paper cited yields the following characteristic relaxation time for a system consisting of a non-conducting medium of dielectric constant ϵ wherein small spheres of a material possessing the same dielectric constant ϵ and the conductivity κ are suspended:

$$\tau = \frac{3 \epsilon_0 \epsilon}{\kappa} \quad (1)$$

Although Wagner's assumptions are but very roughly approximated by Koops' model of ferrite ceramics, by assuming $\kappa = \kappa_\infty \exp \left(-\frac{E}{kT} \right)$ it is nevertheless possible to obtain the grossly correct temperature dependence of the relaxation time:

$$\tau = \tau_\infty \exp \left(\frac{E}{kT} \right) \quad (2)$$

However, a comparison of curves 3 and 5 points to the circumstance that the temperature variations of the point at which maximum losses occur are not related directly to the conductivity, since not all points of discontinuity coincide. This is a hint that relaxation is not related to inhomogeneity of the material. In addition to inhomogeneity, the relaxation observed may reside in a displacement of the ions or electrons. To consider this possibility, it should be stated that Figs. 3 and 5 may serve for determining the activation energies for relaxation and conductivity. They suggest

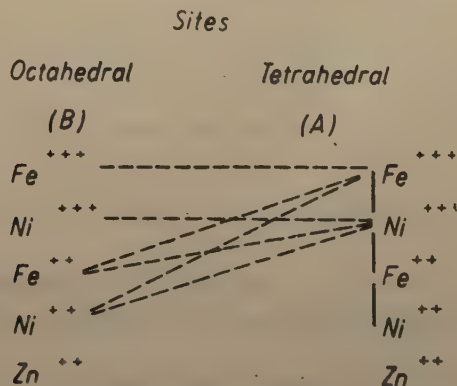


Fig. 6a. Ion distribution over all possible lattice positions.

that the relaxation must be related to electron transitions between ions of different valency, since the conductivity is of electron type and the activation energies differ but very little. Fig. 6a illustrates ion distribution over all possible lattice points. The dashed line denotes antiparallel spin array (negative exchange integral), the continuous line—parallel array of the spins (positive exchange integral) (Néel 1948). Figs. 3 and 5 show that the exchange energy of a pair of ions in the relaxation process must be positive, whereas that of a pair of ions participating in conduction must vanish. The change in activation energy below the Curie point is probably related to the presence of structure-sensitive conduction (Koch and Wagner 1937; de Boer and van Geel 1935; Nijboer 1939). The displacement of this anomaly towards higher temperatures on heating the sample points to the participation of Fe^{++} ions in

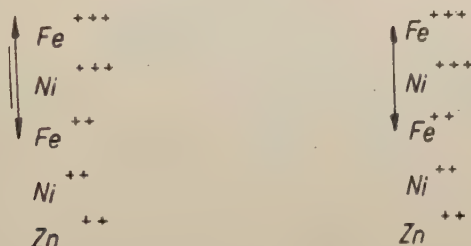


Fig. 6b. Proposed scheme of electron jumps which might explain observed phenomena. Single line — relaxation, double line — conductivity.

both relaxation and conduction. On heating, their number diminishes because of the diffusion of oxygen into the sample (Smolenskiy 1952), and clearly the contribution from defects and impurities begins to play a part.

The foregoing makes it plausible that the most probable scheme of electron transitions is the one illustrated in Fig. 6b. It should be stressed that the possibility of conduction related to electron transitions between ions of iron in the tetrahedral positions has been dismissed, as modern super-exchange theory does not exclude the possibility of $J_{AA} \neq 0$ (Weisz, 1952).

The curves of Figs. 3 and 5 can be described by the following eqs.:

$$\begin{aligned} \varrho &= A_1 \exp \left(\frac{E_1}{kT} \right) + A_2 \exp \left(\frac{E_2}{kT} \right) \\ f &= B_1 \exp \left(- \frac{\varepsilon_1}{kT} \right) + B_2 \exp \left(- \frac{\varepsilon_2}{kT} \right) \end{aligned} \quad (3)$$

The constants $A_{1,2}$ and $B_{1,2}$ may be computed by extrapolating to infinite temperature. Thus, e. g. B_1 and B_2 should be of the orders 10^{11} and 10^{13} , respectively. It is noteworthy that $E_1 \approx \varepsilon_1$, $E_2 \approx \varepsilon_2$.

Another interesting point is that the mechanism of magnetic relaxation is not identical with that of dielectric relaxation, a fact resulting from Fig. 4.

It should be concluded that, at least in the case under consideration, Koops'-theory alone is unable to account for the dielectric properties of ferrites, though the existence or absence of boundary layers has not been decided definitely one way or the other. A good description of the phenomena is obtained if electron diffusion is assumed to be the cause of relaxation.

Results of investigations on other ferrites will be published in the near future.

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GENERAL LAGRANGIAN AND CANONICAL FORMALISM DESCRIBING THE RELATIVISTIC MOTION OF A FREE ROTATING PARTICLE

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The present paper is an endeavour to formulate the problem of the relativistic rotating particle in a Lagrangian form by availing oneself as far as possible of the main results of a previous hydrodynamical theory of the author.

After several attempts to deal with this subject (Aymard 1956, Unal and Vigier 1957; Takabayasi 1958), we have recently set forth, together with P. Hillion and J. P. Vigier (1958), a Lagrangian treatment of the relativistic hydrodynamics of a fluid endowed with intrinsic rotation, the state of this rotation being described by local Einstein—Kramers variables, i. e., by a local rotating tetrad of unitary orthogonal four-vectors. Starting from a well-known variational procedure commonly used in classical field theory (Belinfante 1937; Rosenfeld 1940; Winogradski 1956 and 1959; Halbwachs 1959 — Appendix C), we derived from the usual tensor densities suitable hydrodynamical quantities fulfilling appropriate equations (Halbwachs, Lochak and Vigier 1955, Takabayasi 1957, Halbwachs 1959 — chap. IV). In this procedure one uses a Lagrangian density and its derivatives with respect to the relativistic coordinates x^μ . Such a formalism (as well as all the work hitherto done on spin fluids), has a very abstract and postulatory character, because it is rather difficult to think of a proper or intrinsic rotation in a continuous fluid. It appears thus paradoxical that the much simpler and more concrete problem of the relativistic rotating particle was not yet treated in a Lagrangian form. Such a treatment is just the purpose of the present paper, where we endeavour to carry over the main results of our previous hydrodynamical theory into particle treatment, using a scalar Lagrangian and its proper-time derivative along the world line followed by the particle.

I. Basic vector variables

We shall start here from the idea that a rotating particle is necessarily one with some extent in space, possessing thus an infinite number of degrees of freedom which describe all the details of its structure. In order to express the motion of such

a particle by a finite number of equations, a certain number of global quantities must be introduced by integration over the volume of the particle, the evolution of these global quantities being bound by dynamical equations. The more detailed the description, the more numerous global quantities we shall have to introduce.

We shall base all our considerations on the two following assumptions:

1. All the global quantities to be introduced must be relativistic vectors.
2. A "center" of the particle representing its mean position can be defined.

The particle will thus be described in its internal structure in a more or less detailed manner by a system of vectors localized at its center, in the same way as a function may be described by its Taylor expansion, which accounts more or less accurately for the form of the function in an extended region by means of successive derivatives considered at one point. We shall attempt in these conditions to derive the laws of evolution of the vectors from a suitable Lagrangian formalism and then to build the corresponding canonical formalism.

In a recent paper (Halbwachs and Vigier 1959), we have shown that a Lagrangian founded on the above assumptions and describing a simple particle on which no external field is acting, namely $\mathcal{L}(\dot{x}_\mu, q_\mu^{(r)}, \dot{q}_\mu^{(r)})$ (x_μ denoting the relativistic coordinates of the center of the particle, $q_\mu^{(r)}$ — the vector quantities localized at that point, and the dot standing for the derivative with respect to the proper time τ of the center), yields always two general laws which can be regarded as conservation laws and which are the consequences of the scalar character of the Lagrangian, the principle of stationary integral being taken into account along an arc of the world line followed by the center. We have namely

Conservation of linear momentum:

$$\dot{G}_\mu = 0$$

Conservation of total angular momentum:

$$M_{\mu\nu} = G_\mu \dot{x}_\nu - G_\nu \dot{x}_\mu$$

These laws, which have been known for a long time (Frenkel 1926, Weyssenhoff and Raabe 1947) do not depend on the form of the Lagrangian, nor on the kind and the number of the vectors $q_\mu^{(r)}$ used. The vector G_μ and the antisymmetrical tensor $M_{\mu\nu}$ are expressed by means of the Lagrangian by the formulae

$$G_\mu = \frac{\partial \mathcal{L}}{\partial \dot{x}_\mu},$$

$$M_{\mu\nu} = \dot{q}_\mu^{(r)} \frac{\partial \mathcal{L}}{\partial \dot{q}_\nu^{(r)}} - \dot{q}_\nu^{(r)} \frac{\partial \mathcal{L}}{\partial \dot{q}_\mu^{(r)}}$$

where the summations are to be performed both over the lower tensor indices and over the upper index r labelling the vectors. These expressions are very abstract, and the form of the Lagrangian shall be regarded as adequate only if it leads to giving

them some physical meaning, so that eventually G_μ and $M_{\mu\nu}$ will appear as standing for the physical linear and internal angular momenta.

The main problem to be solved in order to arrive at the Lagrangian is to find the expression of the kinetic rotation energy term. We shall therefore introduce two kinds of physical global quantities, the first kind expressing the rotation in a kinematical way (the global angular velocity), the other kind in a dynamical way (the global angular momentum). The vectors so introduced will be localized both at the "center of matter density" defined by Bohm and Vigier (1958) in their theory of rotating fluid masses.

In order to define the kinematical rotation, we shall first place ourselves in the proper frame of the center of matter density at the instant τ . Let us assume that the extended particle may be looked upon as constituted of a certain number — which may be even infinite — of discrete identical material points, which will describe bare matter, irrespective of the energy (for instance, if the particle is electrically charged, these material points will be assumed to carry equal electric charges and we have to deal then with the distribution and current of electricity). If we then study the spatial distribution of these points and of their instantaneous velocities at the instant τ , we are led to define a system of three orthogonal rotating unitary vectors $\vec{\beta}^{(1)}, \vec{\beta}^{(2)}, \vec{\beta}^{(3)}$, in such a way that the whole of the material points stands on an average at rest with respect to these vectors, so that the instantaneous rotation of this system of vectors at the instant τ describes globally on an average the rotation of the matter of the particle (Halbwachs 1959, chap. V).

The projections of these three vectors on three fixed axes in the proper space make up a matrix C_k^j fulfilling evidently the relations

$$C_k^j C_i^j = \delta_{ki}$$

Its time-derivative will stand for the instantaneous rotation state of the moving triad in the proper space.

The relativistic instantaneous motion will be completely described by the superposition to the above spatial rotation of a Lorentz transformation from the laboratory frame to the proper frame, which includes therefore a relative velocity \vec{v} . Setting

$$\alpha = \left(1 - \frac{v^2}{c^2}\right)^{-\frac{1}{2}}$$

we shall have a unitary velocity u_μ

$$u_j = \alpha v_j, \quad u_4 = \alpha ic \quad (u_\mu u_\mu = -c^2).$$

Along this unitary velocity, we shall take the unit vector

$$b_\mu^{(4)} = u_\mu/ic,$$

that is

$$b_k^{(4)} = \alpha v_k/ic, \quad b_4^{(4)} = \alpha$$

(It is an imaginary time-like vector, with a positive magnitude, imaginary space-components and real time-component in the Minkowski frame).

If we consider the three rotating unit vectors $\vec{\beta}^{(1)}, \vec{\beta}^{(2)}, \vec{\beta}^{(3)}$ in the proper space, we see that they are the projections on the fixed axes in the proper space of three world vectors $b_\mu^{(1)}, b_\mu^{(2)}, b_\mu^{(3)}$, whose projections on the vector $b_\mu^{(4)}$ are zero, and which thus constitute together with the latter an orthogonal tetrad of unitary relativistic four-vectors.

The projections $\beta_k^{(1)}, \beta_k^{(2)}, \beta_k^{(3)}$ are just the matrix elements C_k^j mentioned above, and the relation $C_k^j C_i^j = \delta_{ki}$ merely assures the orthogonality and unitarity of the three vectors in the proper space.

The expression of the four vectors $b_\mu^{(1)}, b_\mu^{(2)}, b_\mu^{(3)}, b_\mu^{(4)}$ with respect to the laboratory frame will be given then by the classical Lorentz transformation (Takabayasi 1958)

$$\begin{aligned} b_j^{(4)} &= \frac{1}{ic} \alpha v_j, & b_4^{(4)} &= \alpha \\ b_4^{(k)} &= \frac{i\alpha v_j}{c} C_j^k, & b_i^{(k)} &= C_i^k + \frac{\alpha^2 v_i v_j}{(1 + \alpha) c^2} C_j^k \end{aligned} \quad (6)$$

These formulae can be looked upon as defining the tetrad $b_\mu^{(\xi)}$ in terms of the ordinary space velocity \vec{v} of the center of the particle with respect to the laboratory frame and of the matrix C_j^k which defines in a conventional way the global proper-space rotation. To summarize, the four world vectors $b_\mu^{(\xi)}$ are the so called Einstein-Kramers variables defining in a kinematical way the global relativistic rotation of the particle. They obey the two equivalent sets of orthogonality and unitarity conditions

$$b_\mu^{(\xi)} b_\nu^{(\xi)} = \delta_{\mu\nu}, \quad b_\mu^{(\xi)} b_\mu^{(\eta)} = \delta^{\xi\eta}.$$

In order to define precisely the global relativistic angular velocity, we start from the elementary treatment of the nonrelativistic dynamics for rigid rotating bodies. It is well known that any rigid rotating body admits at each instant of an axis instantaneously at rest, and the instantaneous rotation state of the body at this instant may be described by an axial vector $\vec{\omega}$ lying along this axis, the so called rotation velocity vector. Two of the Einstein-Kramers vectors, namely $\vec{\beta}^{(1)}$ and $\vec{\beta}^{(2)}$ considered in the proper frame, may be chosen in a plane orthogonal to the instantaneous rotation axis.

We shall have then

$$\vec{\omega} = \frac{d}{dt} \vec{\beta}^{(1)} \times \vec{\beta}^{(1)} = \frac{d}{dt} \vec{\beta}^{(2)} \times \vec{\beta}^{(2)}$$

that is, if we denote by a dot the derivative with respect to the time (which in the proper frame, is just the proper time of the center of matter density)

$$\omega_i = \varepsilon_{ijk} \dot{\beta}_j^{(1)} \beta_k^{(1)} = \varepsilon_{ijk} \dot{\beta}_j^{(2)} \beta_k^{(2)} = \frac{1}{2} \varepsilon_{ijk} (\dot{\beta}_j^{(1)} \beta_k^{(1)} + \dot{\beta}_j^{(2)} \beta_k^{(2)})$$

But it occurs frequently (namely in gyroscopic problems) that it is more suitable to choose the $(\vec{\beta}^{(1)}, \vec{\beta}^{(2)})$ -plane to be orthogonal to some axis $\vec{\beta}^{(3)}$ fixed in the rigid body, such as for instance the inertial axis of a top undergoing a precessing motion. Its velocity has to be superposed to that of the vectors $\vec{\beta}^{(1)}$ and $\vec{\beta}^{(2)}$ and the angular velocity is then given by

$$\omega_i = \frac{1}{2} \varepsilon_{ijk} (\dot{\beta}_j^{(1)} \beta_k^{(1)} + \dot{\beta}_j^{(2)} \beta_k^{(2)} + \dot{\beta}_j^{(3)} \beta_k^{(3)})$$

It is just the latter form we have to choose in order to describe the average rotation of a complex (or eventually fluid) system for which the concept of instantaneous rotation axis does no longer belong to the existence of a set of material points momentarily at rest. We thus write in the proper frame

$$(\omega_i)^0 = \frac{1}{2} \varepsilon_{ijk} (\dot{\beta}_j^{(r)} \beta_k^{(r)})^0,$$

where the summation over $r = 1, 2, 3$ is understood. If we introduce the relativistic four-vectors $b_\mu^{(r)}$ (whose time components are zero in the proper frame)

$$(\omega_i)^0 = \frac{1}{2} \varepsilon_{ijk} (\dot{b}_j^{(r)} b_k^{(r)})^0.$$

Finally, we may add to the sum in the right hand side the homologous term $(\dot{b}_j^{(4)} b_k^{(4)})^0$ owing to the vanishing of the vector $b_k^{(4)}$ in the proper frame. We thus have

$$(\omega_i)^0 = \frac{1}{2} \varepsilon_{ijk} (\dot{b}_j^{(\xi)} b_k^{(\xi)})^0, \quad (\xi = 1, 2, 3, 4).$$

The so called axial vector ω_i considered in the three dimensional space is known to be the dual of an antisymmetrical space tensor, what is brought out in the above expression by the appearance of the symbol ε_{ijk} . In order to pass to the relativistic covariant form, we have to look just upon this tensor as standing for the angular velocity, that is

$$(\omega_{jk})^0 = \frac{1}{2} (\dot{b}_j^{(\xi)} b_k^{(\xi)} - \dot{b}_k^{(\xi)} b_j^{(\xi)}),$$

which is simply

$$(\omega_{jk})^0 = (\dot{b}^{(\xi)} b_k^{(\xi)})^0,$$

the latter tensor being antisymmetrical owing to the orthogonality conditions. This expression may become relativistically covariant by adding (in the proper frame) the homologous term

$$(\omega_{j4})^0 = (\dot{b}_j^{(\xi)} b_4^{(\xi)})^0.$$

As in the proper frame

$$b_4^{(1)} = \dot{b}_4^{(2)} = b_4^{(3)} = 0, \quad b_4^{(4)} = 1;$$

our supplementary term $(\omega_{j4})^0$ reduces to

$$(\omega_{j4})^0 = (b_j^{(4)})^0 = \frac{1}{ic} (\dot{u}_j)^0 = \frac{1}{ic} \left(\frac{dv_j}{dt} \right)^0,$$

that is to the linear acceleration of the center of matter density.

If $(\omega_{jk})^0$ and $(\omega_{j4})^0$ are regarded as the components in the proper space of a relativistic antisymmetrical tensor $\omega_{\mu\nu}$, then we see that the latter embodies at once the rotation of the particle and its acceleration, both properties being brought out as separate components only in the proper frame, while they are inseparably bound together in any other frame.

Finally, we shall introduce as the generalized rotation velocity the relativistic antisymmetrical tensor

$$\omega_{\mu\nu} = \dot{b}_\mu^{(\xi)} b_\nu^{(\xi)}.$$

In order to build the complete expression of the relativistic rotation kinetic energy, we have to introduce yet another set of vector variables expressing the dynamical aspect of the rotation. We shall consider a priori only the cases where this aspect may be described by an antisymmetrical tensor, namely the proper angular momentum $S_{\mu\nu}$, which is just the relativistic generalization of the angular momentum of elementary dynamics. Such an assumption was put forward by all theorists who endowed point-particles with proper rotation (Frenkel 1926, Weyssenhoff and Raabe 1947). It is also by such a tensor that the angular momentum of the electron may be represented, the quantum average value of which is provided by Dirac's theory. The authors who ascribed to the rotating relativistic particle extension in space (Mathisson 1937, Möller 1949, Bohm and Vigier 1958) have also put into evidence similar tensors.

In particular, in Möller's theory the particle is described as a droplet of relativistic classical fluid, characterized at each point by a symmetrical energy-momentum density $t_{\mu\nu}$, the divergence of which vanishes if no external field is acting. Möller introduces then the proper angular momentum density

$$m_{\mu\nu\lambda} = (x_\mu - X_\mu) t_{\nu\lambda} - (x_\nu - X_\nu) t_{\mu\lambda},$$

which is just the moment of $t_{\mu\nu}$ with respect to the so called center of gravity X_μ that is the barycenter of the droplet relative to its energy distribution t_{44} . By integration of $m_{\mu\nu\lambda}$ over the volume of the droplet, one gets the total angular momentum $S_{\mu\nu}$. Bohm and Vigier (1958) follow the same way, but they take as center X_μ the so called center of matter density, which is the barycenter of the distribution of matter (or of electricity). They get thus a more general theory.

Whatever the definition chosen for the tensor $S_{\mu\nu}$, it is always possible to split it in a covariant manner into two relativistic vectors by projecting $S_{\mu\nu}$ and its dual over the unitary velocity (Karpman and Raman 1956, Halbwachs 1957 and 1959 chap. V)

$$u_\mu = ic b_\mu^{(4)}.$$

We thus get the spin

$$s_\mu = \frac{1}{c} \widehat{S}_{\mu\nu} u_\nu = \frac{1}{2} \varepsilon_{\mu\nu\alpha\beta} S_{\alpha\beta} b_\nu^{(4)}$$

and another vector, which we have called the "dullard" (balourd in french)

$$t_\mu = \frac{1}{c} S_{\mu\nu} u_\nu = i S_{\mu\nu} b_\nu^{(4)}$$

These definitions yield for the angular momentum the expression

$$S_{\mu\nu} = v_{\mu\nu\alpha\beta} s_\alpha b_\beta^{(4)} + i (b_\mu^{(4)} t_\nu - b_\nu^{(4)} t_\mu).$$

Obviously

$$s_\mu b_\mu^{(4)} = t_\mu b_\mu^{(4)} = 0.$$

This splitting is profitable as it puts immediately into evidence the important special case where $t_\mu = 0$, it is, the well known Frenkel relation $S_{\mu\nu} u_\nu = 0$, which is introduced as a postulate by most of the authors who have studied the relativistic angular momentum (Frenkel 1926, Costa de Beauregard 1943, Weyssenhoff and Raabe 1949).

Of course the angular momentum, although it describes the rotation in a different way than the angular velocity, is not deprived of any relation with the latter, as it depends after all on the internal motions of the matter inside the extended particle, which also determine the angular velocity. Thus the tensor $S_{\mu\nu}$, although it was introduced irrespective of the vectors $b_\mu^{(\xi)}$, is in fact bound with them through the local variables which describe the details of the structure of the particle. We shall make no detailed assumption about this structure, but we shall be led nevertheless to postulate various kinds of connections between $S_{\mu\nu}$ and the $b_\mu^{(\xi)}$ and this will lead us to various forms of the Lagrangian.

II. Lagrangian formalism

We shall here confine ourselves for the sake of simplicity to the cases where the Lagrangian depends in a linear way upon the derivatives $\dot{b}_\mu^{(\xi)}$ of the Einstein—Kramers variables. As the rotation kinetic energy term is $\frac{1}{2} S_{\mu\nu} \omega_{\mu\nu}$, this assumption will imply that the angular momentum depends only upon the $b_\mu^{(\xi)}$, but not upon their derivatives.

We shall introduce this dependence by successive steps and in a more and more strict way. As a first step let the expression of $S_{\mu\nu}$ depend only upon the vector $b_\mu^{(4)}$ or u_μ , then, as was shown above

$$S_{\mu\nu} = \frac{i}{c} \varepsilon_{\mu\nu\alpha\beta} u_\alpha s_\beta + \frac{1}{c} (u_\mu t_\nu - u_\nu t_\mu) = -S_{\nu\mu}.$$

This expression is just a linear one, and it introduces besides the $b_\mu^{(\xi)}$, two vector variables s_μ and t_μ characterizing dynamically the rotation. We shall thus assume the proper rotation term in the Lagrangian to be

$$\begin{aligned} -\frac{1}{2} S_{\mu\nu} \omega_{\mu\nu} &= -\frac{1}{2} \left[\frac{i}{c} \varepsilon_{\mu\nu\alpha\beta} u_\alpha s_\beta + \frac{1}{c} (u_\mu t_\nu - u_\nu t_\mu) \right] \dot{b}_\mu^{(\xi)} b_\nu^{(\xi)} \\ &= -\frac{1}{2} \left[\frac{i}{c} \varepsilon_{\mu\nu\alpha\beta} u_\alpha s_\beta + \frac{1}{c} (u_\mu t_\nu - u_\nu t_\mu) \right] \dot{b}_\mu^{(r)} b_\nu^{(r)} + \\ &\quad + \frac{1}{2c^2} \left[\frac{i}{c} \varepsilon_{\mu\nu\alpha\beta} u_\alpha s_\beta + \frac{1}{c} (u_\mu t_\nu - u_\nu t_\mu) \right] \dot{u}_\mu u_\nu \end{aligned}$$

(the label r runs from 1 to 3).

We note that, in view of the form of the terms in brackets, if the vectors s_μ and t_μ are split into components respectively orthogonal and parallel to the velocity, the latter will vanish because of the antisymmetry. Thus, the time components do not appear in the Lagrangian and do not interfere in the motion. We may assume therefore the relations

$$s_\mu u_\mu = 0, \quad t_\mu u_\mu = 0$$

to be verified without any restrictions for the motion, and thus we need not introduce any corresponding Lagrange conditions. If these relations and the antisymmetry of $\varepsilon_{\mu\nu\alpha\beta}$ are taken into account, the term with $\dot{u}_\mu u_\nu$ becomes merely

$$\frac{1}{2c} t_\mu \dot{u}_\mu \equiv -\frac{1}{2c} \dot{t}_\mu u_\mu$$

The other terms to be put into the total Lagrangian are the classical Lagrangian $\frac{1}{2} m_0 u_\mu u_\mu$ and a Lagrange term which assures the orthogonality and unitarity conditions, namely

$$\lambda_{\mu\nu} (b_\mu^{(\xi)} b_\nu^{(\xi)} - \delta_{\mu\nu}) = \lambda_{\mu\nu} \left(b_\mu^{(r)} b_\nu^{(r)} - \frac{u_\mu u_\nu}{c^2} - \delta_{\mu\nu} \right),$$

$\lambda_{\mu\nu}$ being an essentially symmetrical Lagrange coefficient. We thus get finally the following Lagrangian

$$\begin{aligned} L &= \frac{1}{2} m_0 u_\mu u_\mu - \frac{1}{2} \left[\frac{i}{c} \varepsilon_{\mu\nu\alpha\beta} u_\alpha s_\beta + \frac{1}{c} (u_\mu t_\nu - u_\nu t_\mu) \right] \dot{b}_\mu^{(r)} b_\nu^{(r)} - \\ &\quad - \frac{1}{2c} \dot{t}_\mu u_\mu + \lambda_{\mu\nu} \left(b_\mu^{(r)} b_\nu^{(r)} - \frac{u_\mu u_\nu}{c^2} - \delta_{\mu\nu} \right). \end{aligned}$$

It is easy to derive the corresponding canonical linear momentum

$$\begin{aligned} G_\mu &= \frac{\partial L}{\partial u_\mu} = m_0 u_\mu - \frac{i}{2c} \varepsilon_{\mu\nu\alpha\beta} \dot{b}_\alpha^{(r)} b_\beta^{(r)} s_\nu - \\ &\quad - \frac{1}{2c} t_\nu (\dot{b}_\mu^{(r)} b_\nu^{(r)} - \dot{b}_\nu^{(r)} b_\mu^{(r)}) - \frac{1}{2c} \dot{t}_\mu - 2 \frac{\lambda_{\mu\nu}}{c^2} u_\nu. \end{aligned}$$

In order to derive the canonical angular momentum, we put

$$\frac{\partial L}{\partial \dot{b}_\mu^{(r)}} = -\frac{1}{2} \left[\frac{i}{c} \varepsilon_{\mu\lambda\alpha\beta} u_\alpha s_\beta + \frac{1}{c} (u_\mu t_\lambda - u_\lambda t_\mu) \right] b_\lambda^{(r)} = -\frac{1}{2} S_{\mu\lambda} b_\lambda^{(r)},$$

$$\frac{\partial L}{\partial \dot{t}_\mu} = -\frac{1}{2c} u_\mu$$

and derive therefrom

$$\begin{aligned} M_{\mu\nu} &= b_\mu^{(r)} \frac{\partial L}{\partial \dot{b}_\nu^{(r)}} - b_\nu^{(r)} \frac{\partial L}{\partial \dot{b}_\mu^{(r)}} + t_\mu \frac{\partial L}{\partial \dot{t}_\nu} - t_\nu \frac{\partial L}{\partial \dot{t}_\mu} \\ &= \frac{1}{2} (S_{\mu\lambda} b_\lambda^{(r)} b_\nu^{(r)} - S_{\nu\lambda} b_\lambda^{(r)} b_\mu^{(r)}) + \frac{1}{2c} (u_\mu t_\nu - u_\nu t_\mu) \\ &= S_{\mu\nu} + \frac{1}{2c^2} (S_{\mu\lambda} u_\lambda u_\nu - S_{\nu\lambda} u_\lambda u_\mu) + \frac{1}{2c} (u_\mu t_\nu - u_\nu t_\mu). \end{aligned}$$

The last line follows from the last but one by taking into account that $b_\lambda^{(r)} b_\nu^{(r)} = \delta_{\lambda\nu} + u_\lambda u_\nu / c^2$. As $S_{\mu\lambda} u_\lambda = ct_\mu$, we get finally

$$M_{\mu\nu} = S_{\mu\nu}.$$

Therefore, the internal angular momentum which is provided by our general formalism is identical with the one we introduced in our Lagrangian in virtue of physical considerations, so that the proposed Lagrangian is suitable for expressing the dynamics of the rotating particle under consideration (with $S_{\mu\nu} u_\nu \neq 0$).

Nevertheless, the two conservation equations which are, as we know, automatically fulfilled

$$\dot{G}_\mu = 0, \quad \dot{S}_{\mu\nu} = G_\mu u_\nu - G_\nu u_\mu$$

are not sufficient for the complete determination of the evolution of the thirteen variables $u_\mu, G_\mu, S_{\mu\nu}$ and not even of the twelve variables $b_\mu^{(\xi)}, s_\mu, t_\mu$ if we take into account the various orthogonality and unitarity relations. (Note that the second set contains one variable less than the first one, because the motion is evidently gauge invariant with respect to any rotation of the $b_\mu^{(1)}, b_\mu^{(2)}$ in the plane orthogonal to the $b_\mu^{(3)}, b_\mu^{(4)}$).

Nevertheless, as the Lagrangian formalism provides just as many Euler equations as the Lagrangian admits of variables, the motion is necessarily determined throughout. It is easy to find the necessary additional equations by taking into account the Euler equations relative to s_μ and t_μ , i. e.,

$$\frac{\partial L}{\partial s_\alpha} \equiv -\frac{i}{2c} \varepsilon_{\mu\nu\alpha\beta} \dot{b}_\mu^{(r)} b_\nu^{(r)} u_\beta \equiv -\frac{i}{2c} \varepsilon_{\mu\nu\alpha\beta} \dot{b}_\mu^{(\xi)} b_\nu^{(\xi)} u_\beta = 0$$

That is

$$\widehat{\omega_{\mu\nu}} u_\nu = 0,$$

$$\frac{\partial L}{\partial t_\mu} - \frac{d}{d\tau} \left(\frac{\partial L}{\partial \dot{t}_\mu} \right) \equiv \frac{1}{2c} u_\nu (\dot{b}_\mu^{(r)} b_\nu^{(r)} - \dot{b}_\nu^{(r)} b_\mu^{(r)}) + \frac{1}{2c} \dot{u}_\mu = 0.$$

As we have

$$u_\nu (\dot{b}_\mu^{(4)} b_\nu^{(4)} - \dot{b}_\nu^{(4)} b_\mu^{(4)}) = \dot{u}_\mu,$$

this yields

$$u_\nu (\dot{b}_\mu^{(\xi)} b_\nu^{(\xi)} - \dot{b}_\nu^{(\xi)} b_\mu^{(\xi)}) = 0,$$

that is

$$\omega_{\mu\nu} u_\nu = 0.$$

In other words, the tensor $\omega_{\mu\nu}$ and its dual are orthogonal to the same vector u_μ . This is only possible if the angular velocity $\omega_{\mu\nu}$ is intrinsically zero. So the proposed Lagrangian stands for a well defined particular case of the general class of motions governed by the system of the ten conservation equations (system of Bohm—Vigier). In that case, the purely kinematical (or electrical) matter of the particle, which differs from its energy, travels as a whole in uniform motion without rotation and acceleration (if no external field is present).

Nevertheless such a particle has a non-vanishing proper angular momentum. This is not inconsistent, as the angular momentum describes the motion of the energy, and in particular the variations of the internal stresses, so that the energy distribution may vary with time without any change of matter distribution, as would do for instance a rotating heat flow inside a fixed solid, inducing a kinetic momentum without any rotation of matter.

If the Bohm — Vigier motion is made more precise by imposing some restriction upon the dynamical variables or by binding the latter more strictly to the kinematical ones then, on the contrary, one will get some kinds of angular velocities less strictly determined.

Thus we may assume (Halbwachs 1957, Bohm and Vigier 1958) t_μ and s_μ to be collinear; this can be expressed by a Lagrange condition $\eta_{\mu\nu} \varepsilon_{\mu\nu\alpha\beta} s_\alpha t_\beta$ or in a more simple way by lessening the number of the variables and putting

$$s_\mu = \sigma_\mu \cos A, \quad t_\mu = \sigma_\mu \sin A.$$

The Euler equations relative to σ_μ and A provide, after some calculation,

$$(\widehat{\omega_{\mu\nu}} \cos A + \omega_{\mu\nu} \sin A) u_\nu = 0.$$

$$(\widehat{\omega_{\mu\nu}} \sin A - \omega_{\mu\nu} \cos A) u_\mu \sigma_\nu = \dot{\sigma}_\mu u_\mu \cos A.$$

We may suppose further (Haibwachs 1959) s_μ and t_μ to be mutually orthogonal and to have the same magnitude s_0 , by introducing the two Langrange terms

$$A s_\mu t_\mu \text{ and } B (s_\mu s_\mu - t_\mu t_\mu)$$

which provide after some calculations

$$\widehat{\omega}_{\mu\nu} u_\nu = \frac{1}{s_0^2} u_\alpha s_\beta (\omega_{\alpha\beta} t_\mu + \omega_{\alpha\beta} s_\mu),$$

$$\omega_{\mu\nu} u_\nu = \frac{1}{s_0^2} u_\alpha s_\beta (\omega_{\alpha\beta} s_\mu - \omega_{\alpha\beta} t_\mu).$$

A more interesting assumption consists in imposing the Frenkel — Weyssenhoff relation $s_{\mu\nu} u_\nu = 0$ which implies that, in the proper frame of the particle (or, more precisely, of its center of matter density), the only non-vanishing components of the angular momentum are the space components. We then get for the thirteen variables $u_\mu, G_\mu, S_{\mu\nu}$ the thirteen equations

$$\dot{G}_\mu = 0, \quad \dot{S}_{\mu\nu} = G_\mu u_\nu - G_\nu u_\mu, \quad S_{\mu\nu} u_\nu = 0$$

which form the so called Weyssenhoff system. This system, which was completely integrated by Weyssenhoff, yields for the thirteen quantities under consideration a well defined law of motion. Nevertheless, it is easy to see that this system is not sufficient for describing all what the Lagrangian tells us about the motion, as it does not inform us about the angular velocity.

The Frenkel — Weyssenhoff condition can be introduced by adding the Lagrange term $A_\mu S_{\mu\nu} u_\nu$. But it is obviously more simple to remove merely in the above Lagrangian the terms containing t_μ , because $t_\mu = S_{\mu\nu} u_\nu / c$ is now zero throughout. The Euler equation for t_μ will then disappear and only the first equation $\partial L / \partial s_\mu = 0$ will remain, that is

$$\widehat{\omega}_{\mu\nu} u_\nu = 0.$$

If we place ourselves in the proper frame, where $u_k^0 = 0$ the latter relation reduces to $\hat{\omega}_{k4}^0 = 0$, that is

$$\omega_{ij}^0 = 0.$$

Thus only the time components of the relativistic angular velocity do not vanish in the proper frame or, in other words, the matter does accelerate but it does not rotate. We note this interesting complementarity between the properties of the angular momentum and those of the angular velocity (Halbwachs. Hillion and Vigier 1958).

The preceding assumption which ascribes to the angular momentum the expression

$$S_{\mu\nu} = \frac{i}{c} \varepsilon_{\mu\nu\alpha\beta} u_\alpha s_\beta = - \varepsilon_{\mu\nu\alpha\beta} b_\alpha^{(4)} s_\beta$$

binds only the dynamical variables to one of the vectors of the kinematical tetrad, namely $b_\mu^{(4)}$. We get another kind of motion if we introduce the supplementary condition that the vector s_μ standing for the spin lies steadily along another of the vectors $b_\mu^{(\xi)}$, let us say for instance $b_\mu^{(3)}$. This result can be obtained either by a Lagrange condition

$$\eta_{\mu\nu} \eta_{\mu\nu\alpha\beta} b_\alpha^{(3)} s_\beta$$

or, in a more simple way, by setting $s_\mu = h_0 b_\mu^{(3)}$ where $h_0 = \sqrt{s_\mu s_\mu}$ is the magnitude of the spin, which is variable in principle.

We get then for the proper rotation term

$$- \frac{i h_0}{2c} \varepsilon_{\mu\nu\alpha\beta} u_\alpha b_\beta^{(3)} \dot{b}_\mu^{(\xi)} \dot{b}_\nu^{(\xi)}.$$

The terms with $\xi = 3$ and $\xi = 4$ are zero because of the antisymmetry, and we are left with

$$\frac{h_0}{2} \varepsilon_{\mu\nu\alpha\beta} b_\alpha^{(4)} b_\beta^{(3)} (\dot{b}_\mu^{(1)} b_\nu^{(1)} + \dot{b}_\mu^{(2)} b_\nu^{(2)}).$$

But we have also between the $b_\mu^{(\xi)}$ the following relations

$$\begin{aligned} \varepsilon_{\mu\nu\alpha\beta} b_\alpha^{(4)} b_\beta^{(3)} b_\nu^{(1)} &= b_\mu^{(2)}, \\ \varepsilon_{\mu\nu\alpha\beta} b_\alpha^{(4)} b_\beta^{(3)} b_\nu^{(2)} &= -b_\mu^{(1)}, \end{aligned}$$

so that we get the expression

$$\frac{h_0}{2} (\dot{b}_\mu^{(1)} b_\mu^{(2)} - \dot{b}_\mu^{(2)} b_\mu^{(1)})$$

or, because of the orthogonality,

$$- h_0 b_\mu^{(1)} \dot{b}_\mu^{(2)}.$$

It follows that the vector $b_\mu^{(3)}$ does no longer appear in the rotation Lagrangian. In order to avoid its redundant appearance in the orthogonality condition it is convenient to replace the form used as yet by the equivalent form

$$\lambda^{\xi\eta} (b_\mu^{(\xi)} b_\mu^{(\eta)} - \delta^{\xi\eta}),$$

where we assume ξ and η to take only the values 1, 2, 4.

Finally, the latter condition being explicitly written down, the Lagrangian becomes

$$\begin{aligned} L = & \frac{1}{2} m_0 u_\mu u_\mu - h_0 b_\mu^{(1)} \dot{b}_\mu^{(2)} + \\ & + \lambda^{11} (b_\mu^{(1)} b_\mu^{(1)} - 1) + \lambda^{22} (b_\mu^{(2)} b_\mu^{(2)} - 1) - \lambda^{44} \left(\frac{u_\mu u_\mu}{c^2} + 1 \right) \\ & + 2\lambda^{12} b_\mu^{(1)} b_\mu^{(2)} + 2 \frac{\lambda^{14}}{ic} b_\mu^{(1)} u_\mu + 2 \frac{\lambda^{24}}{ic} b_\mu^{(2)} u_\mu. \end{aligned}$$

We know already the two conservation relations

$$\dot{G}_\mu = 0, \quad \dot{S}_{\mu\nu} = G_\mu u_\nu - G_\nu u_\mu$$

with

$$G_\mu = \frac{\partial L}{\partial u_\mu}, \quad S_{\mu\nu} = h_0 (b_\mu^{(1)} b_\nu^{(2)} - b_\nu^{(1)} b_\mu^{(2)})$$

(the latter expression being tantamount to $h_0 = \varepsilon_{\mu\nu\alpha\beta} b_\alpha^{(3)} b_\beta^{(4)}$). We shall have also, because of the form of $S_{\mu\nu}$, the Frenkel-Weyssenhoff relation $S_{\mu\nu} u_\nu = 0$. The whole motion, described by means of the dynamical variables, will be the Weyssenhoff motion, but the two variables $b_\mu^{(1)}, b_\mu^{(2)}$ which remain purely kinematical ones, do no longer fulfil the relations of the preceding case.

The three variables $u_\mu, b_\mu^{(1)}, b_\mu^{(2)}$ yield the three Euler equations

$$\left(m_0 - 2 \frac{\lambda^{44}}{c^2} \right) u_\mu + 2 \frac{\lambda^{14}}{ic} b_\mu^{(1)} + 2 \frac{\lambda^{24}}{ic} b_\mu^{(2)} = G_\mu, \quad (1)$$

$$- h_0 \dot{b}_\mu^{(2)} + 2\lambda^{12} b_\mu^{(2)} + 2\lambda^{11} b_\mu^{(1)} + 2 \frac{\lambda^{14}}{ic} u_\mu = 0, \quad (2)$$

$$\dot{h}_0 b_\mu^{(1)} + h_0 \dot{b}_\mu^{(1)} + 2\lambda^{12} b_\mu^{(1)} + 2\lambda^{22} b_\mu^{(2)} + 2 \frac{\lambda^{24}}{ic} u_\mu = 0. \quad (3)$$

If we contract (1) by u_μ , we get

$$G_\mu u_\mu = -m_0 - 2 \frac{\lambda^{44}}{c^2} c^2.$$

On the other hand we note that in all equations obtained by derivation, we meet the difference $m_0 - 2\lambda^{44}/c^2$ and never m_0 or λ^{44} separately. It is thus suitable to put them together in one term. In order to keep m_0 as the proper mass and to assure the unitarity of u_μ , we shall replace both terms $\frac{1}{2} m_0 u_\mu u_\mu$ and $\lambda^{44} (u_\mu u_\mu + c^2)$ by $\frac{1}{2} m_0 (u_\mu u_\mu + c^2)$, m_0 being regarded as a Lagrange multiplier which yields a corresponding Euler equation. We thus get

$$G_\mu^* = m_0 u_\mu + 2 \frac{\lambda^{14}}{ic} \bar{b}_\mu^{(1)} + 2 \frac{\lambda^{24}}{ic} b_\mu^{(2)}, \quad (1')$$

so that

$$G_\mu u_\mu = -m_0 c^2.$$

On the other hand, if we contract (2) by $b_\mu^{(2)}$ we see that $\lambda^{12} = 0$. Hence, the contraction of (3) by $b_\mu^{(1)}$ shows that $\dot{h}_0 = 0$. The magnitude of the spin is constant.

The value of λ^{11} is derived by contracting (2) by $b_\mu^{(1)}$ and that of λ^{22} by contracting (3) by $b_\mu^{(2)}$:

$$\begin{aligned} 2\lambda^{11} &= h_0 b_\mu^{(1)} \dot{b}_\mu^{(2)} b = -2T, \\ \lambda^{11} &= -T, \quad \lambda^{22} = -T. \end{aligned}$$

The value of λ^{11} or λ^{22} stands for the kinetic rotation energy T . If we take into account these results, the three Euler equations may be rewritten in the form:

$$m_0 u_\mu + 2 \frac{\lambda^{14}}{ic} b_\mu^{(1)} + 2 \frac{\lambda^{24}}{ic} b_\mu^{(2)} = G_\mu, \quad (1')$$

$$- h_0 \dot{b}_\mu^{(2)} - 2T b_\mu^{(1)} + 2 \frac{\lambda^{14}}{ic} u_\mu = 0, \quad (2')$$

$$h_0 \dot{b}_\mu^{(1)} - 2T b_\mu^{(2)} + 2 \frac{\lambda^{24}}{ic} u_\mu = 0. \quad (3')$$

We can determine the expression of the two remaining multipliers by contraction of the two last equations by u_μ , which provides

$$2 \frac{\lambda^{14}}{ic} = \frac{h_0}{c^2} b_\mu^{(2)} \dot{u}_\mu, \quad 2 \frac{\lambda^{24}}{ic} = - \frac{h_0}{c^2} b_\mu^{(1)} \dot{u}_\mu$$

and these expressions introduced into (1') give

$$G_\mu = m_0 u_\mu + \frac{h_0}{c^2} (b_\lambda^{(2)} \dot{u}_\lambda b_\mu^{(2)} - b_\lambda^{(1)} \dot{u}_\lambda b_\mu^{(2)}) = m_0 u_\mu + \frac{1}{c^2} S_{\mu\nu} \dot{u}_\nu.$$

This is a well known relation which can be derived directly from Weyssenhoff's laws of motion. Finally by contracting (1') respectively by $b_\mu^{(1)}$ and $b_\mu^{(2)}$, we get

$$G_\mu b_\mu^{(1)} = \frac{h_0}{c^2} b_\mu^{(2)} \dot{u}_\mu = 2 \frac{\lambda^{14}}{ic},$$

$$G_\mu b_\mu^{(2)} = - \frac{h_0}{c^2} b_\mu^{(1)} \dot{u}_\mu = 2 \frac{\lambda^{24}}{ic}.$$

We can finish the determination of the laws governing the kinematical variables by borrowing new results from Weyssenhoff's theory. Let us first recall (Halbwachs 1956) that the spin $s_\mu = h_0 b_\mu^{(3)}$ is a constant vector, as $\dot{s}_\mu = 0$, so that we have $\dot{b}_\mu^{(3)} = 0$. On the other hand u_μ is known to fulfil the following differential equation (Mathisson 1937, Weyssenhoff and Raabe 1949)

$$m_0 \dot{u}_\mu + \frac{1}{c^2} S_{\mu\nu} \ddot{u}_\nu = 0.$$

If $S_{\mu\nu}$ is replaced by $h_0 (b_\mu^{(1)} b_\nu^{(2)} - b_\nu^{(1)} b_\mu^{(2)})$ and if that equation is respectively contracted by $b_\mu^{(1)}$ and $b_\mu^{(2)}$ we get the system

$$m_0 \dot{u}_\mu b_\mu^{(1)} + \frac{1}{c^2} \ddot{u}_\mu b_\mu^{(2)} = 0,$$

$$m_0 \dot{u}_\mu b_\mu^{(2)} - \frac{1}{c^2} \ddot{u}_\mu b_\mu^{(1)} = 0.$$

which determines throughout the motion of $b_\mu^{(1)}$ and $b_\mu^{(2)}$ because u_μ is fully determined by the theory of Weyssenhoff. It is easy to see that these equations are gauge-invariant, that is, they remain valid if $b_\mu^{(1)}$ and $b_\mu^{(2)}$ are respectively replaced by $b_\mu^{(1)} \cos \alpha + b_\mu^{(2)} \sin \alpha$ and $-b_\mu^{(1)} \sin \alpha + b_\mu^{(2)} \cos \alpha$, no matter what value is given to α .

III. Canonical formalism

We shall now use the latter Lagrangian — as the most simple example of a linear Lagrangian — in order to build up a relativistic Hamiltonian formalism for the rotating particle. It is well known that there are two kinds of relativistic Hamiltonians. Let us begin with the scalar Hamiltonian, which will yield covariant canonical equations. Let us first rewrite the Lagrangian

$$L = \frac{1}{2} m_0 (u_\mu u_\mu + c^2) - h_0 b_\mu^{(1)} \dot{b}_\mu^{(2)} + 2 \lambda^{12} b_\mu^{(1)} b_\mu^{(2)} + \\ + 2 \lambda^{11} (b_\mu^{(1)} b_\mu^{(1)} - 1) + 2 \lambda^{22} (b_\mu^{(2)} b_\mu^{(2)} - 1) + 2 \frac{\lambda^{14}}{ic} b_\mu^{(1)} u_\mu + 2 \frac{\lambda^{24}}{ic} b_\mu^{(2)} u_\mu$$

We have obviously as canonical momentum conjugated to x_μ

$$G_\mu = \frac{\partial L}{\partial u_\mu} = m_0 u_\mu + 2 \frac{\lambda^{14}}{ic} b_\mu^{(1)} + 2 \frac{\lambda^{24}}{ic} b_\mu^{(2)}$$

and as canonical momentum conjugated to $b_\mu^{(2)}$

$$\beta_\mu^{(2)} = \frac{\partial L}{\partial \dot{b}_\mu^{(2)}} = -h_0 b_\mu^{(1)}.$$

Thus $\beta_\mu^{(2)}$ happens to appear already in the Lagrangian. For simplicity of notation we shall omit from now on some upper indices by putting

$$b_\mu^{(2)} = b_\mu, b_\mu^{(1)} = -\frac{\beta_\mu}{h_0}, S_{\mu\nu} = b_\mu \beta_\nu - b_\nu \beta_\mu.$$

As regards the other variables, as their derivatives do not appear, they provide merely the customary Euler equations and their conjugated momenta are permanently zero, so that they bring no contribution to the Hamiltonian. The Euler equations would have to appear as the corresponding canonical equations.

Moreover, to simplify writing, we shall put

$$\frac{\lambda^{24}}{ic} = l', -\frac{\lambda^{14}}{ic h_0} = l, \lambda^{11} = T, \frac{\lambda^{22}}{h_0^2} = T', -\frac{\lambda^{12}}{h_0} = \lambda.$$

Thus the Hamiltonian, derived by a Legendre transformation whose generating function is the Lagrangian, will take the form

$$H = G_\mu \dot{u}_\mu + \beta_\mu \dot{b}_\mu - L(G_\mu, b_\mu, \beta_\mu, m_0, l, l', T, T', \lambda)$$

with the canonical equations

$$\begin{aligned}\frac{\partial H}{\partial G_\mu} &= u_\mu, & \frac{\partial H}{\partial \beta_\mu} &= \dot{b}_\mu, \\ \frac{\partial H}{\partial x_\mu} &= 0 = -\dot{G}_\mu, & \frac{\partial H}{\partial b_\mu} &= -\dot{\beta}_\mu, \\ \frac{\partial H}{\partial m_0} &= \frac{\partial H}{\partial l} = \frac{\partial H}{\partial l'} = \frac{\partial H}{\partial T} = \frac{\partial H}{\partial t'} = \frac{\partial H}{\partial \lambda} = 0.\end{aligned}$$

By expressing L in terms of the canonical variables, we get without difficulty

$$\begin{aligned}H &= G_\mu u_\mu + \beta_\mu \dot{b}_\mu - \frac{1}{2} (G_\mu - 2l' b_\mu - 2l \beta_\mu) u_\mu - \frac{1}{2} m_0 c^2 - \beta_\mu \dot{b}_\mu - \lambda b_\mu \beta_\mu - \\ &\quad - T(b_{\mu\mu} - 1) - T'(\beta_\mu \beta_\mu - h_0^2) - 2l' u_\mu b_\mu - 2l u_\mu \beta_\mu = \\ &= -\frac{1}{2} m_0 c^2 + \frac{1}{2} G_\mu u_\mu - \lambda b_\mu \beta_\mu - l' b_\mu u_\mu - l \beta_\mu u_\mu - T(b_\mu b_\mu - 1) - \\ &\quad - T'(\beta_\mu \beta_\mu - h_0^2).\end{aligned}$$

That is, after replacing u_μ by its expression

$$\begin{aligned}H &= \frac{1}{2m_0} [(G_\mu - 2l' b_\mu - 2l \beta_\mu)^2 - m_0^2 c^2] - \\ &\quad - T(b_\mu b_\mu - 1) - T'(\beta_\mu \beta_\mu - h_0^2) - \lambda b_\mu \beta_\mu.\end{aligned}$$

The canonical equations relative to G_μ and x_μ provide

$$\begin{aligned}\frac{\partial H}{\partial G_\mu} &\equiv \frac{1}{m_0} (G_\mu - 2l' b_\mu - 2l \beta_\mu) u_\mu \\ \dot{G}_\mu &= 0.\end{aligned}\tag{4}$$

This is the expression for the linear momentum and the first Weyssenhoff equation. Taking into account the first canonical equation (4), the six remaining canonical equations provide the four already known results

$$\begin{aligned}\frac{\partial H}{\partial m_0} &\equiv -\frac{1}{2} u_\mu u_\mu - \frac{c^2}{2} = 0, \text{ (that is } u_\mu u_\mu = -c^2), \\ \frac{\partial H}{\partial l} &\equiv -2\beta_\mu u_\mu = 0, \quad \frac{\partial H}{\partial l'} \equiv -2b_\mu u_\mu = 0 \\ \frac{\partial H}{\partial T} &\equiv -(b_\mu b_\mu - 1) = 0, \quad \frac{\partial H}{\partial T'} \equiv -(\beta_\mu \beta_\mu - h_0^2) = 0, \\ \frac{\partial H}{\partial \lambda} &\equiv -b_\mu \beta_\mu = 0,\end{aligned}$$

being the orthogonality and unitarity relations, and

$$\begin{aligned}\frac{\partial H}{\partial \beta_\mu} &\equiv -2l u_\mu - 2T' \beta_\mu - \lambda b_\mu = \dot{b}_\mu, \\ \frac{\partial H}{\partial b_\mu} &\equiv -2l' u_\mu - 2T b_\mu - \lambda \beta_\mu = -\dot{\beta}_\mu.\end{aligned}$$

The expressions for the subsidiary variables l , l' , T , T' , λ are obtained by contraction of the two latter equations respectively by u_μ , b_μ , and β_μ , the orthogonality and unitarity relations being taken into account,

$$\begin{aligned}l &= \frac{1}{2c^2} \dot{b}_\mu u_\mu, & l' &= -\frac{1}{2c^2} \dot{\beta}_\mu u_\mu, \\ T' &= -\frac{1}{2h_0^2} \dot{b}_\mu \beta_\mu, & T &= \frac{1}{2h_0^2} \dot{\beta}_\mu b_\mu = T', \\ \lambda &= -\dot{b}_\mu b_\mu = \dot{\beta}_\mu \beta_\mu = 0.\end{aligned}$$

By substituting these expressions into the complete equations, we get two following equations

$$\begin{aligned}\dot{b}_\mu &= -\frac{1}{c^2} \dot{b}_\nu u_\mu \cdot u_\nu + \frac{1}{h_0^2} \dot{b}_\nu \beta_\mu \cdot \beta_\nu \\ \dot{\beta}_\mu &= -\frac{1}{c^2} \dot{\beta}_\nu u_\mu \cdot u_\nu + \dot{\beta}_\nu b_\mu \cdot b_\nu.\end{aligned}$$

By translation into the tetrad symbolism, these equations become

$$\begin{aligned}\dot{b}_\mu^{(2)} &= (\dot{b}_\nu^{(2)} b_\nu^{(4)}) \cdot b_\mu^{(4)} + (\dot{b}_\nu^{(2)} b_\nu^{(1)}) \cdot b_\mu^{(1)} \\ \dot{b}_\mu^{(1)} &= (\dot{b}_\nu^{(1)} b_\nu^{(4)}) \cdot b_\mu^{(4)} + (\dot{b}_\nu^{(1)} b_\nu^{(2)}) \cdot b_\mu^{(2)}.\end{aligned}$$

Thus the derivative $\dot{b}_\mu^{(2)}$ reduces to its projections on $b_\mu^{(1)}$ and u_μ , and the derivative $\dot{b}_\mu^{(1)}$ to its projections on $b_\mu^{(2)}$ and u_μ . The components of both derivatives parallel to $b_\mu^{(3)}$ vanish and thus we are led once more to the result that the spin $s_\mu = h_0 b_\mu^{(3)}$ of the free Weyssenhoff particle is constant in time. The corresponding equation $\dot{b}_\mu^{(3)} = 0$ is equivalent to the second Weyssenhoff equation.

Finally it is useful to write down the Hamiltonian equations in canonical form by elimination of the subsidiary variables l , l' , T , T' and λ . Equation (4) contracted respectively by b_μ and β_μ provides

$$l' = \frac{1}{2} G_\mu b_\mu, \quad l = \frac{1}{2h_0^2} G_\mu \beta_\mu.$$

Thus the canonical equations become

$$\begin{aligned}\dot{G}_\mu &= 0, \quad G_\mu - G_\nu b_\nu \cdot b_\mu - \frac{G_\nu \beta_\nu}{h_0^2} \beta_\mu = m_0 \dot{x}_\mu, \\ G_\nu b_\nu \left(G_\mu - G_\lambda b_\lambda \cdot b_\mu - \frac{G_\lambda \beta_\lambda}{h_0^2} \beta_\mu \right) &= \dot{\beta}_\nu (\delta_{\mu\nu} - b_\mu b_\nu), \\ \frac{G_\nu \beta_\nu}{h_0^2} \left(G_\mu - G_\lambda b_\lambda \cdot b_\mu - \frac{G_\lambda \beta_\lambda}{h_0^2} \beta_\mu \right) &= -\dot{b}_\nu \left(\delta_{\mu\nu} - \frac{\beta_\mu \beta_\nu}{h_0^2} \right).\end{aligned}$$

This Hamiltonian formalism is very suitable for putting into evidence the constants of the motion with the aid of classical Poisson brackets. It is easy to verify that we have, besides the constancy of G_μ ,

$$[G_\mu u_\mu, H] = 0$$

expressing the constancy of the proper mass, and

$$[\varepsilon_{\mu\nu\alpha\beta} u_\nu b_\alpha \beta_\beta, H] = 0$$

expressing the constancy of the spin vector (and of course of its magnitude). For these calculation u_μ has evidently to be expressed in terms of the canonical variables.

We shall finally construct the non-covariant Hamiltonian \mathcal{H} leading to non-covariant canonical equations expressed in terms of the derivatives with respect to the time $t = x_4/ic$. It is well known that \mathcal{H} will then stand for the particle energy with respect to the considered frame of reference.

We see easily that if we substitute the above canonical equations in the expression of the scalar Hamiltonian H , we get $H = -m_0 c^2$. Then, if we write the latter equation as a relation between the sixteen canonical variables, we may consider one of these variables, namely G_4 , as being a function of the fifteen remaining ones. We put therefore

$$\mathcal{H} = -ic G_4(x_k, G_k, b_\mu, \beta_\mu, t)$$

and get

$$\frac{\partial \mathcal{H}}{\partial x_k} = -\frac{dG_k}{dt}, \quad \frac{\partial \mathcal{H}}{\partial G_k} = \frac{dx_k}{dt}, \quad \frac{\partial \mathcal{H}}{\partial t} = \frac{d\mathcal{H}}{dt}, \quad \frac{\partial \mathcal{H}}{\partial b_\mu} = -\frac{d\beta_\mu}{dt}, \quad \frac{\partial \mathcal{H}}{\partial \beta_\mu} = \frac{db_\mu}{dt}.$$

If we write down explicitly H with separate space and time components, we obtain

$$\begin{aligned}H &\equiv \frac{1}{2m_0} \left[G_k - \frac{G_r \beta_r - G_4 \beta_4}{h_0^2} \beta_k - (G_r b_r + G_4 b_4) b_k \right]^2 + \\ &+ \frac{1}{2m_0} \left[G_4 - \frac{G_r \beta_r - G_4 \beta_4}{h_0^2} \beta_4 - (G_r b_r + G_4 b_4) b_4 \right]^2 - \\ &- \frac{1}{2} m_0 c^2 + \frac{1}{2} \beta_\lambda \dot{\beta}_\lambda \left(\frac{\beta_\mu \beta_\mu}{h_0^2} + b_r b_r - 2 \right) = -m_0 c^2\end{aligned}$$

and finally if we replace G_4 by $i\mathcal{H}/c$, we get

$$\begin{aligned} & \left[G_k - \frac{G_r \beta_r - \mathcal{H} \beta_4 / ic}{h_0^2} \beta_k - (G_r b_r - \mathcal{H} b_4 / ic) b_k \right]^2 + \\ & + \left[\frac{\mathcal{H}}{ic} + \frac{G_r \beta_r - \mathcal{H} \beta_4 / ic}{h_0^2} \beta_4 + (G_r b_r - \mathcal{H} b_4 / ic) b_4 \right]^2 \\ & = -m_0^2 c^2 - m_0 \beta_\lambda \dot{b}_\lambda \left(\frac{\beta_\mu \beta_\mu}{h_0^2} + b_\mu b_\mu - 2 \right) \end{aligned}$$

It is not necessary to derive \mathcal{H} explicitly from that equation as we are only concerned with its derivatives, which can be easily obtained by differentiating the equation itself and considering \mathcal{H} as a function of the canonical variables $x_k, t, G_k, b_\mu, \beta_\mu$

1) If the variables x_k and t appear nowhere explicitly, the corresponding canonical equations $\partial\mathcal{H}/\partial x_\mu = -dG_\mu/dt$ yield

$$\frac{dG_k}{dt} = 0 \quad \text{and} \quad \frac{d\mathcal{H}}{dt} = 0.$$

Thus, in the case when no external force is acting, the particle momentum and its energy are constant in time.

2) Let us now take the derivative with respect to G_k :

$$\begin{aligned} & 2 \left(G_\mu - \frac{G_\lambda \beta_\lambda}{h_0^2} \beta_\nu - G_\lambda b_\lambda \cdot b_\nu \right) \left[-\frac{\beta_k \beta_\nu}{h_0^2} - b_k b_\nu + \frac{1}{ic} \left(\frac{\beta_4 \beta_\nu}{h_0^2} + b_4 b_\nu \right) \right] \frac{\partial \mathcal{H}}{\partial G_k} + \\ & + 2 \left(G_k - \frac{G_\lambda \beta_\lambda}{h_0^2} \beta_k - G_\lambda b_\lambda \cdot b_k \right) - \frac{2}{ic} \left(G_4 - \frac{G_\lambda \beta_\lambda}{h_0^2} \beta_4 - G_\lambda b_\lambda \cdot b_4 \right) \frac{\partial \mathcal{H}}{\partial G_k} = 0, \\ & \frac{1}{ic} \frac{\partial \mathcal{H}}{\partial G_k} \left[G_4 - \frac{G_\lambda \beta_\lambda}{h_0^2} \beta_4 - G_\lambda b_\lambda \cdot b_4 - \left(\frac{\beta_4 \beta_\nu}{h_0^2} + b_4 b_\nu \right) \left(G_\nu - \frac{G_\lambda \beta_\lambda}{h_0^2} \beta_\nu - G_\lambda b_\lambda \cdot b_\nu \right) \right] \\ & = G_k - \frac{G_\lambda \beta_\lambda}{h_0^2} \beta_k - G_\lambda b_\lambda \cdot b_k - \left(\frac{\beta_k \beta_\nu}{h_0^2} + b_k b_\nu \right) \left(G_\nu - \frac{G_\lambda \beta_\lambda}{h_0^2} \beta_\nu - G_\lambda b_\lambda \cdot b_\nu \right). \end{aligned}$$

Now, if we take into account the orthogonality and unitarity relations, we see that the last term in bracket and the last term on the right-hand side both vanish. So we are left with

$$\frac{\partial \mathcal{H}}{\partial G_k} = ic \frac{G_k - \beta_k \cdot G_\lambda \beta_\lambda / h_0^2 - b_k \cdot G_\lambda b_\lambda}{G_4 - \beta_4 \cdot G_\lambda \beta_\lambda / h_0^2 - b_4 \cdot G_\lambda b_\lambda}.$$

If we remember that

$$G_\mu - \beta_\mu \cdot G_\lambda \beta_\lambda / h_0^2 - b_\mu \cdot G_\lambda b_\lambda = m_0 u_\mu,$$

we see that

$$\frac{\partial \mathcal{H}}{\partial G_k} = ic \frac{u_k}{u_4} = ic \frac{v_k}{ic} = v_k,$$

v_k being the nonrelativistic velocity dx_k/dt . We thus see that we just find again the canonical equation

$$\frac{\partial \mathcal{H}}{\partial G_k} = \frac{dx^k}{dt}.$$

3) Let us take now the derivative with respect to b_μ , the factor $m_0 \beta_\lambda \dot{b}_\lambda$ being dropped, as it vanishes in virtue of the orthogonality relations. So we get

$$\begin{aligned} G_\lambda b_\lambda \left(G_\mu - \frac{G_\lambda \beta_\lambda}{h_0^2} \beta_\mu - G_\lambda b_\lambda \cdot b_\mu \right) + G_\mu b_\nu \left(G_\nu - \frac{G_\lambda \beta_\lambda}{h_0^2} \beta_\nu - G_\lambda b_\lambda \cdot b_\nu \right) + \\ + \frac{1}{ic} \frac{\partial \mathcal{H}}{\partial b_\mu} \left(G_4 - \frac{G_\lambda \beta_\lambda}{h_0^2} \beta_4 - G_\lambda b_\lambda \cdot b_4 \right) - \frac{1}{ic} \frac{\partial \mathcal{H}}{\partial b_\mu} \left(G_\nu - \frac{G_\lambda \beta_\lambda}{h_0^2} \beta_\nu - G_\lambda b_\lambda \cdot b_\nu \right) \left(\frac{\beta_4 \beta_\nu}{h_0^2} + b_4 b_\nu \right) = m_0 \beta_\lambda \dot{b}_\lambda \cdot b_\mu. \end{aligned}$$

Then, if the orthogonality relations are taken into account, we get

$$\frac{\partial \mathcal{H}}{\partial b_\mu} = -ic \frac{G_\nu b_\nu (G_\mu - \beta_\mu \cdot G_\lambda \beta_\lambda / h_0^2 - b_\mu \cdot G_\lambda b_\lambda) - m_0 \beta_\lambda \dot{b}_\lambda \cdot b_\mu}{G_4 - \beta_4 \cdot G_\lambda \beta_\lambda / h_0^2 - b_4 \cdot G_\lambda b_\lambda}.$$

A very similar calculation provides the derivative with respect to β_μ :

$$\frac{\partial \mathcal{H}}{\partial \beta_\mu} = -ic \frac{(G_\nu \beta_\nu / h_0^2) (G_\mu - \beta_\mu \cdot G_\lambda \beta_\lambda / h_0^2 - b_\mu \cdot G_\lambda b_\lambda) - m_0 \beta_\mu \cdot \beta_\lambda \dot{b}_\lambda / h_0^2}{G_4 - \beta_4 \cdot G_\lambda \beta_\lambda / h_0^2 - b_4 \cdot G_\lambda b_\lambda}.$$

It will be remembered that in these expressions $G_4 = i\mathcal{H}/c$ is constant in time. As for the factors $\beta_\lambda \dot{b}_\lambda = -\dot{\beta}_\lambda b_\lambda$, which contain proper time derivatives, they can be easily expressed in terms of db_λ/dt and $d\beta_\lambda/dt$ by introducing $\alpha = (1 - v^2/c^2)^{-\frac{1}{2}}$ if one remembers that

$$\begin{aligned} \alpha ic = u_4 = G_4 - \beta_4 \cdot G_\lambda \beta_\lambda / h_0^2 - b_4 \cdot G_\lambda b_\lambda, \\ \dot{\beta}_\lambda = \alpha \frac{d\beta_\lambda}{dt} = \frac{1}{ic} (G_4 - \beta_4 \cdot G_\lambda \beta_\lambda / h_0^2 - b_4 \cdot G_\lambda b_\lambda) \cdot \frac{d\beta_\lambda}{dt}. \end{aligned}$$

This provides finally

$$\begin{aligned} \frac{\partial \mathcal{H}}{\partial b_\mu} = -ic G_\nu b_\nu \frac{G_\mu - \beta_\mu \cdot G_\lambda \beta_\lambda / h_0^2 - b_\mu \cdot G_\lambda b_\lambda}{G_4 - \beta_4 \cdot G_\lambda \beta_\lambda / h_0^2 - b_4 \cdot G_\lambda b_\lambda} - m_0 b_\mu \cdot \beta_\lambda \frac{db_\lambda}{dt} \\ \frac{\partial \mathcal{H}}{\partial \beta_\mu} = -ic \frac{G_\nu \beta_\nu}{h_0^2} \frac{G_\mu - \beta_\mu \cdot G_\lambda \beta_\lambda / h_0^2 - b_\mu \cdot G_\lambda b_\lambda}{G_4 - \beta_4 \cdot G_\lambda \beta_\lambda / h_0^2 - b_4 \cdot G_\lambda b_\lambda} - m_0 \frac{\beta_\mu}{h_0^2} \cdot \beta_\lambda \frac{d\beta_\lambda}{dt}. \end{aligned}$$

By replacing $G_\mu - G_\lambda \beta_\lambda \cdot \beta_\mu / h_0^2 - G_\lambda b_\lambda \cdot b_\mu$ by $m_0 \alpha v_\mu$ the Hamilton equations become

$$- G_\nu b_\nu \cdot v_\mu - \frac{d\beta_\lambda}{dt} b_\lambda \cdot b_\mu = - \frac{d\beta_\mu}{dt},$$

$$- G_\nu \beta_\nu \cdot \frac{v_\mu}{h_0^2} + \frac{db_\lambda}{dt} \beta_\lambda \cdot \frac{\beta_\mu}{h_0^2} = \frac{db_\mu}{dt}.$$

That is

$$\frac{d\beta_\lambda}{dt} (\delta_{\lambda\mu} - b_\lambda b_\mu) = G_\lambda b_\lambda \cdot v_\mu,$$

$$\frac{db_\lambda}{dt} \left(\delta_{\lambda\mu} - \frac{\beta_\lambda \beta_\mu}{h_0^2} \right) = - \frac{G_\lambda \beta_\lambda}{h_0^2} v_\mu,$$

which gives just again, after multiplication by α , the covariant equations (5) which are equivalent to the second Weyssenhoff equation.

IV. Conclusion

In the present paper we have limited ourselves to very simple cases, as well with regard to the external field, which was assumed to be zero, as concerning the form of the Lagrangian, which was chosen to be linear. Nevertheless our formalism can be very useful for several purposes. For instance, we can attempt to frame a fluid endowed with intrinsic rotation with an underlying particle structure admitting of a chaotic motion. We can approach this problem with the methods of statistical mechanics which are known to require a Hamiltonian formalism. The above non-covariant Hamiltonian will be convenient in the framework of classical statistics, based on the use of a definite frame of reference. But it would be perhaps possible to remain in a covariant formalism by using a generalized phase space with the variables x_μ , G_μ , b_μ , β_μ . For this purpose our covariant Hamiltonian formalism may prove very useful.

On the other hand, by passing from the present classical formalism to a quantal one by means of the usual quantization methods, we can put into evidence some new wave equations connected with the spin concept.

I am indebted to Mr. J. P. Vigier and to Mr. T. Takabayasi for many helpful discussions.

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LETTERS TO THE EDITOR

IN—PILE HALL COEFFICIENT MEASUREMENTS OF GERMANIUM BOMBARDED BY FAST NEUTRONS

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Lattice defects produced by fast neutron bombardment introduce localized energy states into the forbidden energy band of germanium. This causes the change of *n*-type germanium into *p*-type germanium when irradiated by fast neutrons. In order to investigate the nature of this fast neutron bombardment in the neighbourhood of the intrinsic region, a semi-continuous in-pile Hall coefficient measurement was made. A small electromagnet (placed in an experimental hole of our swimming-pool type reactor) and an automatic recording measurement facility were used, and both the Hall coefficient and conductivity were measured. The results obtained can be seen in Fig. 1. The initial conductivity of the *n*-type samples was about $0.5 \text{ ohm}^{-1} \text{ cm}^{-1}$, and the final one of the *p*-type obtained after 20 hours of irradiation (in a fast neutron flux of about $3.10^{10} \text{ cm}^{-2} \text{ sec}^{-1}$) was about $0.15 \text{ ohm}^{-1} \text{ cm}^{-1}$. Because a small dose of fast neutrons was used, it was reasonable to assume that no measurable changes in mobilities and scattering factors were caused. On this assumption, the Hall coefficient curve was calculated on the basis of a two-carrier model from the conductivity curve, provided that the ratio of the electron to hole mobility was 2.05. The obtained discrepancy can be seen in Fig. 2.

A fairly good fit can be obtained by introducing a three-carrier model. The presence in germanium of two types of holes of different effective masses has been indicated by cyclotron resonance experiments¹ and verified by magnetoresistance and Hall measurements in *p*-type germanium.² Recently Walton and Moos³ indicated that the assumption of 2% of light holes leads to a mobility of these holes which is six times greater than that of ordinary ones. In the described experiment the good fit shown

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in Fig. 2 was obtained with the same percentage of light holes, and the light to ordinary holes mobility ratio equals 6.5. In this way we get by a different experiment an additional argument in favour of the results obtained by the authors mentioned above

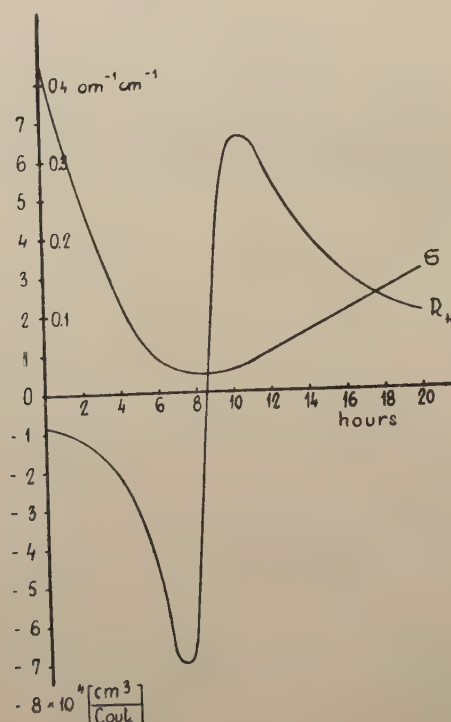


Fig. 1. Electrical conductivity and Hall coefficient R_H vs. time of fast neutron irradiation

(see Table I). Some measurements of the Hall coefficient in different magnetic fields also support these assumptions. Further work is under way.

The authors are deeply indebted to Dr H. Rzewuski of this laboratory for discussion and criticism.

TABLE 1

Authors	T	Percentage of light holes	Light to ordinary holes mobility ratio
Dresselhaus, Kipp, and Kittel ¹	4°K	—	7.5
Willardson, Harman, and Beer ²	300°K	2 %	8
Walton and Moos ³	300°K	2 %	6
Ours	300°K	2 %	6.5

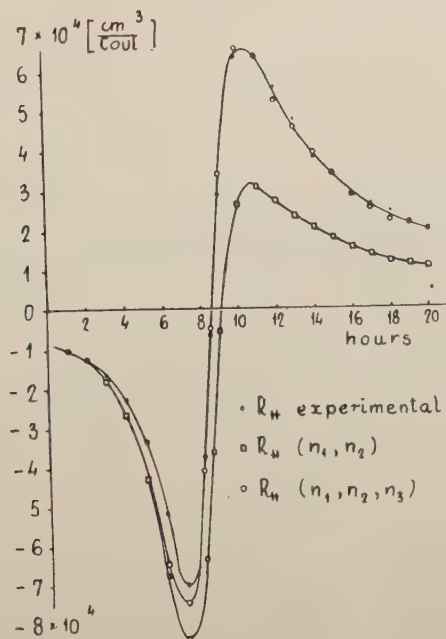


Fig. 2. Hall coefficient vs. time of fast neutron irradiation: dots — experimental points, squares — calculated on the basis of a two — carrier model, circles — calculated on the basis of a three — carrier model

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STATISTICAL SIGNIFICANCE OF DOUBLE MAXIMUM ANGULAR DISTRIBUTION IN HIGH ENERGY JETS

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In previous papers of our group^{1, 2, 3} it was found that the angular distributions of secondary particles emitted in collisions of high energy nucleons ($> 10^{12}$ eV) with nucleons or nuclei showed the characteristic shape: in coordinates dN/dx vs x_i , where $x_i = \log \tan \Theta_i$ (Θ_i are the angles of the secondary particles with the primary direction) the distribution have two symmetrical maxima. On the contrary the hydrodynamical theories predicted Gaussian distributions, both for nucleon-nucleon and nucleon-nucleus collisions. In order to explain the observed shape of the distributions we introduced the two-centre model, as we have called it. (See also^{4, 5}). In recent times several authors have discussed this model⁶. Since the introduction of the two-centre model was mainly based on the existence of double maximum distributions and since on the other hand there were some objections concerning the statistical significance of this fact⁷, we decided to report here the results of a statistical analysis of the angular distributions. This analysis was performed on the full available collection of jets generated in photographic emulsions by single nucleons of energy higher than 10^{12} eV. The total number of jets was 56*.

The hydrodynamical theories for both nucleon-nucleon and nucleon-nucleus collisions predict an increase of the anisotropy (in terms of the dispersion σ) with increasing energy, the shape of the distribution remaining a Gaussian one, independently of the energy. Therefore we could normalize all distributions to one Gaussian distribution. We performed this normalization for all 56 events and the results are shown in Fig. 1 as a differential histogram. The intervals on the x -axis correspond to equal areas for the Gaussian distribution. For this distribution we obtain a straight horizontal line. The deviation from the Gaussian shape is clearly visible on the figure

* Jets from our laboratories, from published papers, and from different laboratories. We are very much obliged to Professor N. Dobrotin for kindly sending us the angular distributions of jets from collaborating laboratories and to Dr. D. H. Perkins for the material from H. H. Wills Laboratory, Bristol.

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